Journal of Thermal Analysis, Vol. 46 (1996) 643-679

THERMAL ANALYSIS OF MACROMOLECULES
A personal review

B. Wunderlich

Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600 and
Division of Chemical and Analytical Sciences, Oak Ridge National Laboratory, Oak Ridge,
TN 37831-6197, USA

Abstract

This review traces the development of thermal analysis over the last 40 years as it was experienced and contributed to by the author. The article touches upon the beginning of calorimetry and thermal analysis of polymers, the development of differential scanning calorimetry (DSC), single run DSC and other special instrumentations, up to the recent addition of modulation to calorimetry. Many new words and phrases have been introduced to the field by the author and his students, leaving a trail of the varied interests one can have over 40 years. It began with "cold crystallization" and most recently the term "oriented, intermediate phase" was coined, creating in-between: "extended chain crystals," the "irreversible thermodynamics of melting of polymer crystals," "dynamic differential thermal analysis" (DDTA), "the rule of constant increase of C_p per mobile bead within a molecule at the glass transition temperature," "superheating of polymer crystals," "melting kinetics," "crystallization during polymerization," the "chain-folding principle, "molecular nucleation," "rigid amorphous phase," a "system of classifying molecules," "macroconformations," "amorphous defects," "rules for the entropy of fusion based on molecular shape and flexibility," "single-molecule single-crystals," "a system of classifying phases and mesophases," and "condis phase."

Keywords: DDTA, DSC, macromolecules

A. Introduction

A Brief Biography

It is a special honor to be asked by the editor to add a personal review of Thermal Analysis of Macromolecules to this special issue of the Journal of Thermal Analysis that recognizes my 65th birthday. At the same time this is also the 50th anniversary of my interest in Chemistry and the 40th anniversary of the beginning of my work in thermal analysis and polymer science. It is amazing how fast time passes when one has fun with what one is doing.

It all began somewhat sadly with the bombing of the house of my parents on April 20, 1945 in Brandenburg, Germany. Fortunately the family was not at home. We were refugees in the forests nearby. After the war had ended and some degree of normalcy had returned, school started again in the Fall of 1945,

0368-4466/96/ $ 5.00

John Wiley & Sons, Limited
Chichester

but my goal to become a farmer needed to be revised due to the land reform introduced in East Germany. It took my prospective farm and left no other choice but to continue my education through the high school level.

In 1946 I discovered chemistry by reading the 9th edition of U. Hofmann's "Inorganic Chemistry." The book had ended up the year before in my collection when the two floors of our apartment building collapsed during the bombing. Our neighbor, who used the book in his studies, thought I might enjoy studying it. I did. What an enormous source of interesting facts and historical footnotes! Later, I could use the same textbook at the University of Berlin (Humboldt University, 1949–53) as the basic study guide. In 1947, chemistry was introduced as a high-school subject, and being properly primed, I made it quickly to the top of the class in this subject, and ultimately chose it for my university study in 1949. The 14th edition of Hofmann (and Ruedorf) is still on my book shelf and over the years has answered many questions in chemistry.

The beginning of the university study was, again, not without some problems. It took the forceful intervention of Professor Thilo of the Humboldt University to overcome the problem that I did not belong to the preferred class of workers and peasants and was not politically active. Besides teaching me how to teach chemistry, Professor Thilo instilled an interest in phosphates and silicates. Many years later a student of mine and I could contribute to his journal some new knowledge about "crystallization during polymerization" of LiH_2PO_4, using thermogravimetry (TGA) and differential scanning calorimetry (DSC) [1].

After four years, my wish to solely study chemistry and avoid politics made me a refugee again [on June 17, 1953, the date of the uprising in the GDR (East Germany)]. With Professor Thilo's help I could at least extract my proof of study from Berlin. After a few months in refugee camps and work at the Farbwerke Hoechst, I continued studying chemistry for two semesters at the Goethe University in Frankfurt, got married in the famous City Hall (the Römer), and emigrated to the United States.

Two semesters of study at Hastings College in Hastings, NE taught me everything needed to enter graduate school as Research Assistant to Prof. Malcolm Dole at Northwestern University in Evanston, IL. The subject of study was calorimetry of polymers. It was a very opportune time for this topic. Polymers was still a relatively new subject, taught at very few universities, and calorimetry has always been a topic for only a select few researchers. Professor Dole, being a former coworker in Debye's Institute in Leipzig, Germany in 1929, and having gained interest in polymers already before WW II, was the unique expert in the field to educate students [2]. Under his expert guidance it took until 1957 to complete my Ph.D. thesis on "Thermodynamics of the Copolymer System Poly(ethylene terephthalate-sebacate)" [3, 4]. Besides the actual heat capacity measurements, the process of "cold crystallization" was recognized and named. It occurs somewhat above the glass transition temperature as the limiting nonequilibrium mode of crystallization. During a subsequent year as Instructor at Northwestern University, the kinetics, thermodynamics, and statistics of the nonequilibrium cold crystallization and melting were analyzed with help of the, at that time, revolutionary electronic calculator (IBM 650) [5]. Figure 1 illustrates the broad area of possible nonequilibrium crystallinity if one assumes that cold crystallization in polyterephthalates is limited to nanocrystals of three repeating units in length (≈3 nanometers).

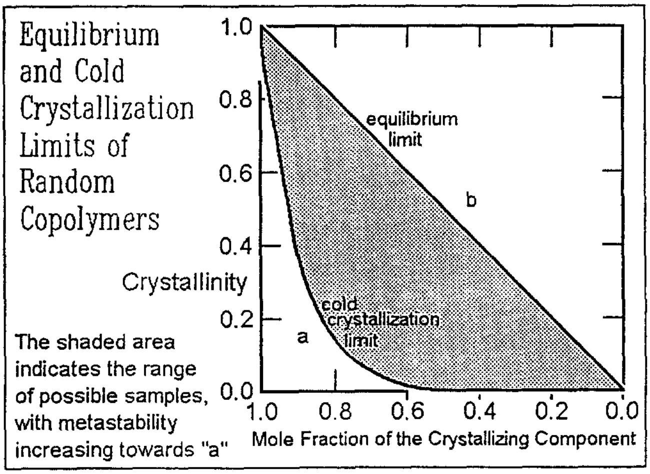

Fig. 1 Mass fraction crystallinity w_c of component A in poly(A-*co*-B) after cold crystallization as function of mole fraction of A. Curve a is the lower limit of nonequilibrium crystallinity. Curve b indicates the equilibrium crystallinity [5]

Many of the present research topics of our Advanced THermal Analysis System and Laboratory, ATHAS, have their roots in this first look at the thermal properties of polymers. Further early work was carried out at Cornell University where I was an instructor and later assistant professor in the Department of Chemistry from 1958 to 1963 (Sect. B, below). The main body of research was generated during my 25 year tenure at Rensselaer Polytechnic Institute (1963–88) as Professor of Chemistry (promotion to full professor in 1965) (Sects. C, and D). After early retirement from RPI, the next stage of research was begun at The University of Tennessee and at Oak Ridge National Laboratory (1988–today). This most recent work is covered mainly in Sect. E and continues at a rapid pace, building on all prior experience. The idea of the ATHAS was generated in the mid 1970's and has ever since been the focus of the research of my students and postdoctoral fellows.

B. Early calorimetry and knowledge about solid polymers (1955–1965)

Most calorimetry on polymers was in this early time period done by adiabatic calorimetry. The instrumentation was based on the classical design of Nernst [6]. Major calorimeters were only in operation at the Bureau of Standards [7] (now NIST) and Prof. Dole's laboratory [8]. During this decade these two major producers of data on polymers were joined by the GE Research Laboratory (Karasz *et al.* [9]) and work was begun at the University of Leeds, England (Dainton *et al.* [10]). A check of the literature [11] revealed that through 1955 only 30 papers on heat capacity of linear macromolecules were published, describing mainly natural and synthetic rubbers, polystyrene, poly(vinyl chloride), polyethylene, selenium, nylon 6, poly(tetrafluoroethylene), and poly(fluorotrichloroethylene). The first papers on heat capacity of characterized polymers date back to 1928 [12], 1935 [13], 1937 [14] and 1938 [15]. The basis of the theory of heat capacity of solids was given by Einstein [16] and Debye [17], and an extension to polymers was suggested by Tarasov [18]. A detailed analysis of the vibrational characteristics of a polymer was suggested by Stockmayer and Hecht [19]. This means that at that time a solid foundation existed for the growth of thermal analysis of polymers. The major limitation was that most attempts to understand the thermal properties of macromolecules used an equilibrium approach and that the morphology of polymer crystals was not well understood.

The knowledge of flexible macromolecules in the solid state underwent a dramatic change in this time period. Polymers with rather regular chemical structure were known to crystallize, but only partially. Less regular polymers were glassy at sufficiently low temperature. Both states of matter are not in equilibrium [20]. With the help of electron microscopy it could be shown in 1955 by Keller, Fischer, Till, and Kobayashi that flexible macromolecules are prone to crystallize in a lamellar morphology [21]. The polymer molecules are much longer than the lamellae are thick and fold or leave the crystal phase at the lamellar surface. The lamellar thickness (fold length) was found to be 5–50 nm, making the crystals highly metastable. Optical interference microscopy [22] was developed in our laboratory for quantitative analysis of the morphology and measurement of lamellar thickness [23]. Extending the measurements to solution-grown single crystals produced at pressures up to 600 MPa gave experimental proof that the reason for chain folding was kinetic and not thermodynamic. By covering a 100 K range of crystallization temperatures, the lamellar thickness was found to change with supercooling and not with temperature [24].

The experience with crystallization under elevated pressure led to the discovery of "extended chain crystals" of polyethylene [25]. At pressures above about 300 MPa, linear polyethylene melts would, after crystallization to folded-chain lamellae, anneal to a thickness that could reach the molecular lengths of typically 1–10 μm and also achieve close to 100% crystallinity. These observations meant that, given the right experimental conditions, the whole spectrum from metastable to equilibrium crystals could be produced and was in need to be studied by thermal analysis.

For thermal analysis it was necessary to learn how to deal with the metastability of solid polymers. As the melting point is approached, annealing, reorganization and recrystallization to higher stability is possible, i.e. the sample may change during calorimetry. The first solutions were to run calorimeters as fast as possible and avoid the intermittent stops needed for regaining equilibrium [26, 27]. The next step was to build new calorimeters for smaller masses adapted better to continuous heating [28]. Finally, in 1960, continuous differential calorimetry for masses as little as one gram, and with heating rates as fast as 1.0 K min^{-1} was demonstrated by Müller and Martin [29]. About five years later, two radically new commercial calorimeters were introduced, the differential scanning calorimeters (DSC) by the Perkin-Elmer Corp. Norwalk, CT [30] and the DuPont Instrument Division, Wilmington DE (now TA Instruments, Inc.). These instruments permitted quantitative measurements for masses as little as 10 mg and with heating rates as fast as 40 K min^{-1}. Such DSCs are the principal tools for the analysis of metastable and unstable states.

Before the development of commercial DSCs we adapted differential thermal analysis, DTA, to the measurement of heat (calorimetry) [31], as we had adapted before the calorimeter to measure heat continuously [26]. For the first time it became possible to show by thermal analysis that the unusually large specific surface free energy (J g^{-1}) of the thin lamellar crystals of polyethylene can cause a substantial decrease in melting temperature [31]. It could also be proven that the fold surfaces introduced additional, and often the major melting point lowering in copolymers [32]. This insight into the "irreversible thermodynamics of melting of polymer crystals" was summarized in two basic papers on defect polymer crystals. These papers were finally published in England despite many objections from referees who did not grasp the importance of nonequilibrium processes [33]. A path of zero-entropy-production melting using fast heating was proposed, in opposition to the generally accepted slow heating. The rationale was to achieve a quick transition from the metastable crystal to the equally metastable melt. Slow heating, in contrast, brings changes in perfection of the crystals and, as a result, may suggest erroneously high melting points.

The other metastable state, the glass, was also analyzed in our laboratory. A special, sequential heating and cooling method was invented for the DTA, a method that we called "Dynamic Differential Thermal Analysis" or DDTA [34]. The kinetics of the freezing of polystyrene was derived mathematically [35] and compared to the DDTA experiments, using the hole model of the liquid state, as applied to polymers by Hirai and Eyring [36]. It could be demonstrated that the glass transition temperature T_g changes logarithmically with cooling rate, and that the hysteresis (enthalpy relaxation) can be described mathematically. The rather cumbersome equations could be solved with the help of an electronic computer. Studying all of the available calorimetric data on the change of the heat capacity, C_p, at T_g allowed us to formulate "the rule of constant increase of C_p per mobile bead within a molecule at the glass transition temperature" [37]. This rule states that every flexible part of a molecule (bead), has a heat capacity increase of about 11 J/(K mol of beads). It permits the estimation of the flexibility of a molecule by thermal analysis, and also documents that the change in heat capacity at the glass transition temperature is an extensive thermodynamic quantity and can be used to find the amount of amorphous material in a multi-phase material.

Besides metastable states, the equilibrium state is always in need to be well characterized since it forms the limit against which the metastable state must be assessed. Heat capacities are the basis of all thermal properties and are in this characterization most important. The total heat content, H, is not measurable directly. It must be measured by summation of all the incremental amounts of heat capacity [$C_p = (\mathrm{d}H/\mathrm{d}T)_{p,n}$, heat added per kelvin at constant pressure, p and composition, n]:

$$H(T) = H(T_o) + \int_{T_o}^{T} C_p \, \mathrm{d}T \qquad (1)$$

This equation underscores the importance of either to measure heat capacity over the whole temperature range, or to develop a theory that allows extrapolation of limited data. This latter approach was taken in our laboratory for the evaluation of the heat capacity of solids (glasses and crystals).

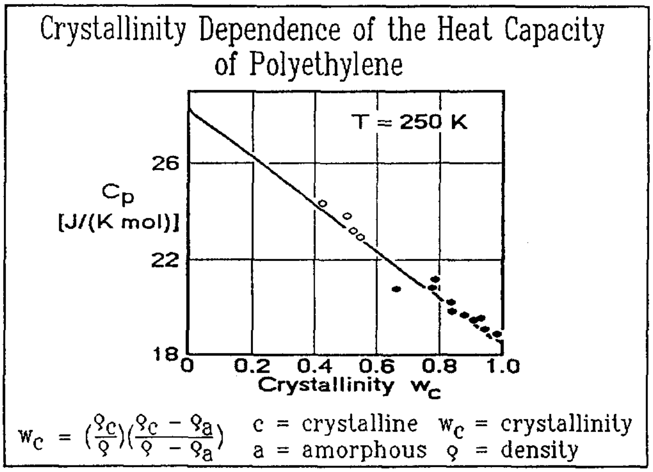

Fig. 2 Extrapolation of heat capacity to the crystal and glass. (Filled circles refer to linear polyethylene, open circles to branched)

In the solid state the heat capacity is caused almost entirely by vibrational energy. Based on the work by Einstein [16], Debye [17], and Tarasov [18], an approximate vibrational spectrum was fitted by us to the heat capacities that are known often only over a limited temperature range. Polyethylene was the first fully analyzed sample [38]. The experimental heat capacities [26] were combined with all literature values to a data-set that could be extrapolated to 100% crystallinity, as shown in Fig. 2. The limiting extrapolated heat capacities are given in Fig. 3. The fit to the approximate frequency spectrum is shown in its later, final form in Fig. 4 [39]. For the first time the measured equilibrium thermal properties could be linked to a vibrational spectrum to understand the

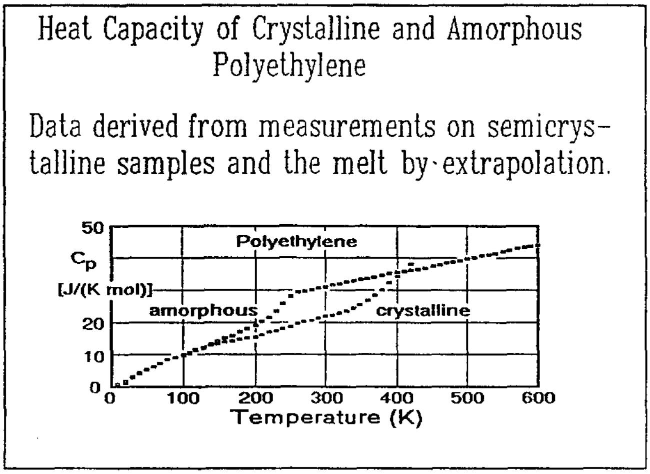

Fig. 3 Heat capacity limits as gained from extrapolation

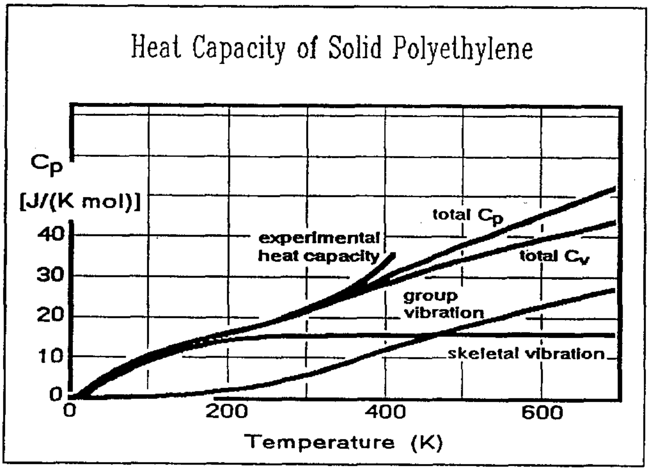

Fig. 4 Contributions to the heat capacity of polyethylene

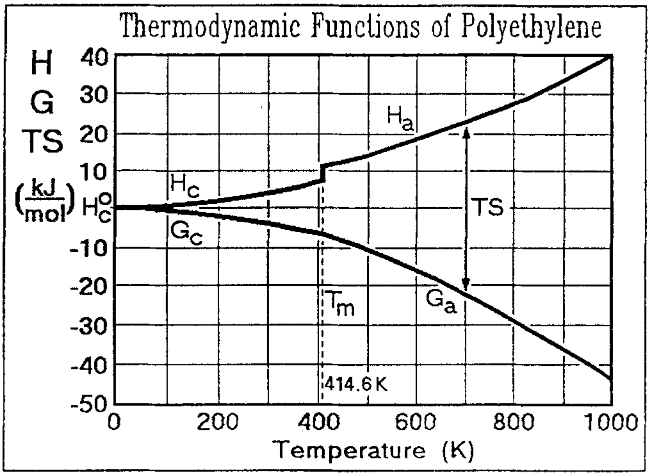

Fig. 5 Enthalpy, *H*, free enthalpy, *G*, and entropy *S* (as *TS*); subscript a =amorphous, c =crystal)

motion in the solid state of high polymers [40]. It was then also possible to give quantitative information for the crystals on the degree of order, *via* the entropy *S*, and the stability, *via* the free enthalpy *G*:

$$S(T) = S(T_o) + \int_{T_o}^{T} \frac{C_p}{T}\,\mathrm{d}T \tag{2}$$

$$G = H - TS \tag{3}$$

Figure 5 displays the final result. This first analysis has led over the years to similar analyses of over 200 polymers and polymer-related materials.

Figure 3 displays also the heat capacity of the amorphous state (crystallinity 0%). At high temperature this is the melt, at low temperature the glass. The glassy state is quite difficult to reach for the fast crystallizing polyethylene, but Fig. 3 displays clearly the glass transition temperature of 237 K. Of special interest is also the rather gradual beginning of the glass transition, starting at about 120 K. This was explained as a slow beginning of local conformational motion (*gauche-trans* equilibrium) on the basis of estimates of the energy and by interpretation of mechanical properties and NMR data [41].

These first ten years of research in polymer morphology and thermal properties confirmed the value of full analyses of materials using structure and energy considerations. It became clear that the two roots of the full description of materials are their mass and energy. Quantitative methods for the measurement of mass and energy were equally well developed at the beginning of modern science, some 200 years ago [42]. Based on the constancy of combining ratios of the masses of elements in chemical reactions, Dalton [43] could prove the atomic theory of matter. This started the development that today lets us "see" molecules in full structural detail. The magnification factor to go from the atomic scale (0.1 nm or 1 Å) to the macroscopically visible scale (1 μm) is 10^4. While the research into the mass of matter took now a path to find more and more structural detail on an atomic, microscopic level, the research into the energetics went in the direction of a macroscopic description through thermodynamics [44]. Its link to molecular motion was limited largely to the description of ideal gases ($pV = nRT = 1/3M\overline{v}^2$ where $\overline{v}^2$ is the mean square particle velocity). The reason for this preference of macroscopic description of the energetics is the even larger scaling factor needed to "visualize" molecular motion in the condensed states. This feat became only possible in the last few years through simulation of crystals on supercomputers [45]. The molecular time scale for large-amplitude motion is in the picosecond range (10^{-12} s). Compared to the fastest directly observable processes that take perhaps one millisecond (10^{-3} s), one needs a scaling factor of 10^9! This is much further removed from human experience than the structure information. The understanding of the link of molecular motion to thermal and mechanical properties is only now developing rapidly.

C. First differential scanning calorimetry and morphology research (1965–1975)

The availability of commercial DSC equipment that was far superior to any self-built instruments falls into the beginning of this time period. We bought our first Perkin-Elmer DSC-1 in 1965 and repeated the polyethylene measurements on the now available completely crystalline and extended chain crystals within a few days work [46]. The quality of the data rivaled even those gained by adiabatic calorimetry [26]. Coupled with dilatometry, the equilibrium melting temperature T_m^o could be fixed within a fraction of a kelvin to be 414.6 K and the difference between equilibrium and nonequilibrium dissolution temperatures could be used to estimate the surface free energy γ (0.083 J m^{-2}) using the Thomson-Gibbs equation [47]:

$$\Delta T = \frac{2\gamma\, T_m^o}{\Delta h_f\, \rho l} \tag{4}$$

where Δh_f is the heat of fusion (293 J g^{-1}), ρ, the density (1.0 Mg m^{-3}), and l the lamellar thickness. A lamella of 10 nm thickness has a specific surface area of 200 m^2 g^{-1} and leads to a ΔT of 23.5 K. The enormous surface areas of polymer crystals explain most of their metastability. This straightforward experimentation revealed two additional important facts. First, the heat capacity of polyethylene is what one would expect from extrapolation of paraffin data.

Later research detailed that the continuous change in C_p with chain length is due to a steady increase in skeletal vibration frequencies, starting with solid hexane [48]. Second, extended-chain crystals melt rather slowly and can lead to "superheating of polymer crystals," i.e. melting is slower than the conduction of the heat of fusion into the sample [49]. A new field of study was initiated, the "kinetics of melting," to be contrasted to the kinetics of crystallization. This topic was also our contribution to the First and Second International Congresses on Thermal Analysis at Aberdeen, Scotland and Worcester, MA in 1965 and 1968, respectively (ICTA) [50]. In Aberdeen, our contribution was one of only five in the field of polymer science (131 papers, overall). Things have changed over the years, polymer science is by now the main contributor to thermal analysis, chiefly due to the easy availability of DSC and its capability of high precision.

The about 100 publications that were generated from 1965 to 1975 at RPI can be summarized in six major topics that are discussed next with key citations: 1.) The work on "extended-chain crystals" was continued [51]. 2.) It led to the study of "crystallization during polymerization" [52]. 3.) This, in turn led to the discovery of "molecular nucleation" [53]. 4.) A number of polymers besides polyethylene were analyzed. 5.) The glass transition of pressure-densified polymers was measured. 6.) A major effort was made to write-up completed subjects as books or book chapters [11, 21, 54] and a new teaching method, that of the Audio Courses was experimented with [55]. All throughout, thermal analysis was providing the direction for new research and basis of better information on materials.

The knowledge gained on extended-chain crystals was the key for the understanding of metastability in polymer crystals, polyethylene being the model for all flexible macromolecules [51]. We originally thought seeding with equilibrium crystals might help in growing more stable crystals, but it just did not work [56]. Thermal analysis showed that there is only little enhancement of crystallization due to the presence of this most perfect crystal substrate. It was also shown in this research that folded chain crystals are initially less perfect and anneal subsequently at the crystallization temperature to a more perfect state [56]. Towards the completion of crystallization, lower-melting crystals form. These observations suggest limits of the classical theory of polymer crystal growth which is based on single-step addition of segments that span the full lamellar thickness [21, Vol. 2]. Morphological details of the nucleation, growth, annealing, and melting were generated by electron microscopy [57, 58]. The distribution of the observed nuclei excluded the commonly assumed utility of secondary nucleation in crystal growth. Obvious locations of secondary nuclei were ignored by the molecules on crystallization. Experiments on polypropylene and computer simulations led Binsbergen to quite similar conclusions [59]. Secondary nucleation does not seem to govern the crystallization rate.

The mechanism of chain extension on crystallization of polyethylene under elevated pressure provided another puzzle. From the microcopy of the crystals and the thermal analysis of melting it was clear that the initial crystal had to be chain folded [51]. The chain extension had to be a subsequent annealing step [58]. Why, however, does the more restrictive crystallization under high pressure permit chain extension? This question was resolved in two stages. First Bassett observed in 1972 that at elevated pressures, sufficient for chain-extension for polyethylene, a hexagonal phase is stable [60]. The corresponding phase diagram is shown in Fig. 6. We could later identify this hexagonal phase as conformationally disordered, as a "condis crystal" [61]. Only condis crystals have the required high mobility for the fast diffusion of the chains through the crystal for full chain extension. Although not all flexible polymers that crystallize into a condis phase anneal to extended-chain crystals, all extended-chain crystals grown from the polymer melt are condis crystals [62]. Pressure, in turn, is not a prerequisite. Examples, of other extended chain crystals are poly(tetrafluoroethylene), poly(chlorotrifluoroethylene), poly(diethylsiloxane) and *trans*-1,4-polybutadiene.

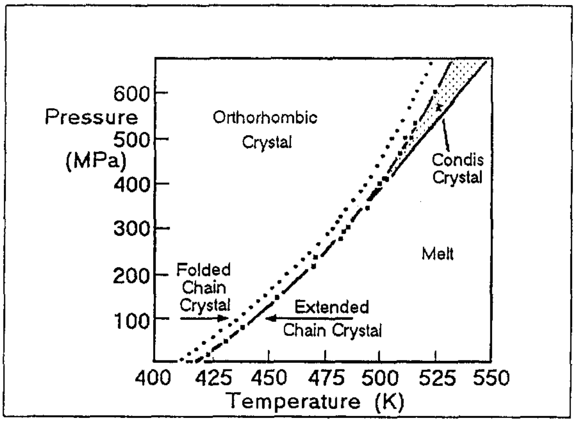

Fig. 6 Phase diagram of polyethylene

Having observed initial chain folding even for extended-chain crystals, I felt certain that one can formulate a "chain-folding principle" [21, Vol. I, p. 193]: "A sufficiently regular, flexible linear macromolecule crystallized from the mobile, random state will always crystallize first in a chain-folded macroconformation." This chain-folding principle has naturally a corollary. It should be possible to grow extended chain crystals directly on "crystallization during polymerization," bypassing the polymeric, random state. My first sabbatical leave 1966/67 at the University of Mainz was used to investigate this question [52]. Many indications that extended chain crystals of polymers can grow from the monomer were already in the literature, and a series of examples were analyzed by us in the following years (selenium from the vapor [51, VII and IX], poly(oxymethylene) from trioxane [63], polyparaxylylene from the cyclic paraxylylene dimer [64], polyethylene from diazomethane [65], lithium polyphosphate from lithium dihydrogen phosphate [1], and poly(tetrafluoroethylene) from gaseous fluoroethylene [51, VIII]. For more details see also [21, Vol. 2]. Figure 7 shows the schematic of extended chain crystal growth of poly(oxymethylene) inside a single crystal of trioxane. Similar simple mechanisms can often lead to fully extended equilibrium crystals of flexible macromolecules. A large number of intermediate cases where crystallization occurs shortly after polymerization have also been identified. In these cases the degree of chain folding is an indicator of the separation of polymerization and crystallization in location and time. This turned out to be specially important for the discussion of biological syntheses as in celluloses and silks, for example [21, 52]. The crystallization during polymerization provides also the bridge to the knowledge of crystallization of small molecules.

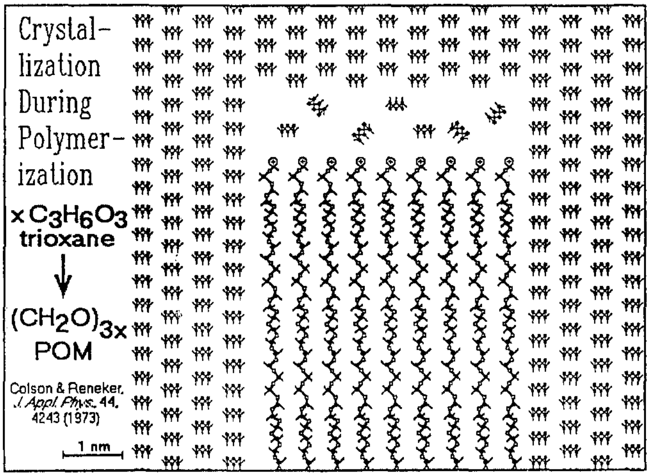

Fig. 7 Schematic of crystallization of poly(oxymethylene) during polymerization

It was suggested above that secondary nucleation was not the rate-determining step in crystallization of flexible polymers. If it is not, what takes its place? The crystallization kinetics of all analyzed flexible polymers had shown an exponential crystallization rate, dependent on the inverse of the supercooling, a clear sign of some type of nucleation control [21]. This seeming contradiction is not yet fully resolved, but a qualitative discussion can be given as follows: Plots of melting and crystallization rates *vs.* temperature exhibit a break, as shown in Fig. 8. The kinetics is not continuous through the equilibrium melting temperature, in contrast to the Onsager's principle of microscopic reversibility. There is a region of metastability below the equilibrium melting temperature where the melt is metastable. Even seeding with stable crystals does not break this metastability [56]. Our study of crystallization indicated, in addition, that a growing crystal in a melt of a broad distribution of molar masses can reject with

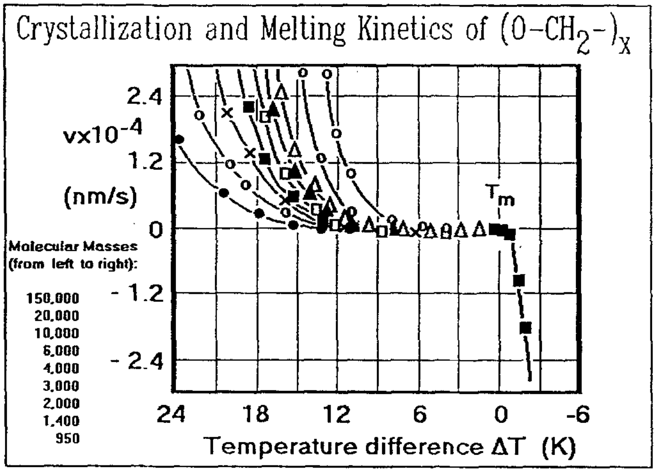

Fig. 8 Illustration of the break between crystallization and melting kinetics for poly(oxyethylene)

perfect selectivity molecules of sizes that are sufficient to lead to stable crystals [66]. Such segregation must have a reversible step. Our suggestion is that there must be a "molecular nucleation" step [53, 67]. The molecular nucleus involves, depending on supercooling, all or a portion of every molecule as the first step of crystallization. This molecular nucleation provides the rate-limiting step [21]. This proposal maintains the proper rate dependence of crystal growth (Fig. 8), explains the molecular mass segregation, and satisfies the reversibility of crystallization/melting, but now on a single-molecule level. Once a molecular nucleus exists, melting and crystallization are reversible on the molecular scale. If the molecule is completely removed from the crystal surface, new molecular nucleation with the necessary supercooling is required, explaining the break in Fig. 8. Although a quantitative description of molecular nucleation is still outstanding, all of the many experimental results observed seem to be in qualitative agreement with the molecular nucleation concept. Besides the model polyethylene [53, 66] an even more complete analysis was carried out later on poly(oxyethylene) [68].

The detailed thermal analysis beyond polyethylene began with poly(oxymethylene) [63]. Superheating, double and triple melting peaks, crystal perfection on heating, recrystallization, annealing, and ultimately decomposition could be observed. A general free enthalpy diagram was derived that permits to visualize the metastable states and their transitions, as shown in Fig. 9. All the indicated transitions could be documented and their special signature in thermal analysis was derived. Other polymers studied included poly(ethylene terephthalate), of interest because of its ease of change of the backbone structure through etching and solid state polymerization [69]; selenium, a polymer that can open

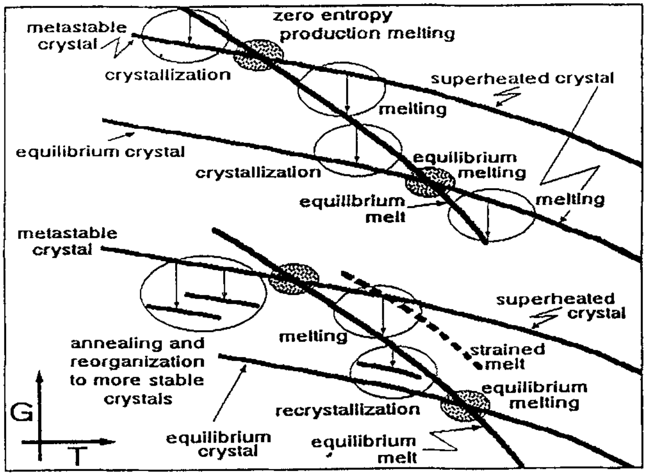

Fig. 9 Free enthalpy diagram to correlate the various equilibrium and nonequilibrium states of polymer crystals. Upper diagram: Melting and crystallization. Lower diagram: Annealing, reorganization, recrystallization, and melting into a strained melt. Upward transitions between the states are forbidden by the second law (ΔG must be negative or zero)

its folds to anneal to extended chain crystals [70]; polyparaxylylene, that shows several polymorphs and can be crystallized during or immediately after crystallization [71]; polycaprolactam (nylon 6) that can also be polymerized into the solid state [72]; and poly(tetrafluoroethylene), a molecule with an intriguing polymorphism [73]. Another compound that caught our interest was a tetraalkyl ammonium salt [74]. More will have to be said later about this compound and its mesophases.

The work on glass transitions was continued with a study of the hysteresis for glucose, selenium, poly(vinyl chloride), polystyrene, poly(methyl methacrylate), and poly(oxy-2,6-dimethyl-1,4-phenylene) (PPO) [75]. The parameters for the kinetic description [35] were determined. As expected, low- and high-molar-mass compounds behaved similarly. What was not expected was that densified glasses obtained on vitrification under elevated pressure did not have a lower enthalpy. On annealing they showed a relaxation that needed different relaxation times for dilatometry and calorimetry [76]. This precludes a description of the glass transition as a solely free volume or entropy governed process, something that is frequently done to reach a simple description. Intermediate between molecules or parts of molecules in crystalline and amorphous phases are tie molecules which bridge between crystals. Their presence could be proven by DSC coupled with selective dissolution [77].

This large volume of new information needed to be fit into an overall picture. A second sabbatical was spent entirely in the library at RPI to complete a trea-

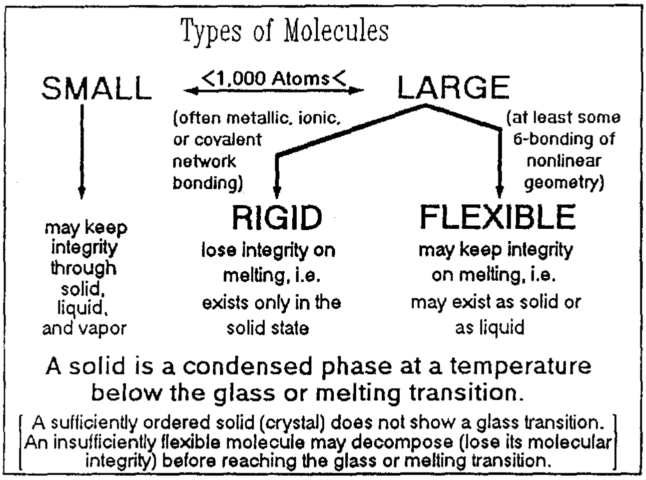

Fig. 10 Summary of the all types of molecules

tise on macromolecular physics [21]. The flexible macromolecules were placed into a general "system of classifying molecules," as shown in Fig. 10. Another clarification introduced was the nomenclature for the shape of flexible macromolecules as a whole: the "macroconformation." The term macroconformation is distinct from the term conformation which describes the limited arrangement about one or several bonds (also called rotational isomerism) and the term morphology which describes the shape of the crystal. The limiting macroconformations of polymers are identified in Fig. 11.

The summary of the emerging knowledge about defects of polymers as described in [21, Vol. 2] led to the introduction of the idea of "amorphous

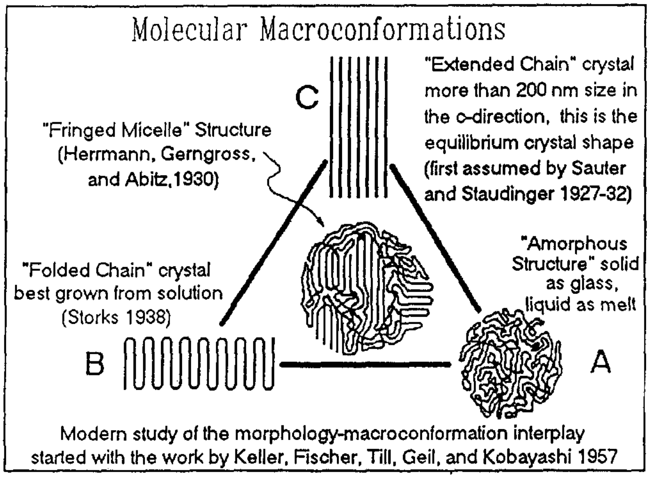

Fig. 11 Molecular macroconformations that describe the shape of polymer molecules

defects." An amorphous defect is a three-dimensional defect, caused by molecules that are partially included in the crystal. It is thus a phase, but of nanometer size. Initially it was assessed only by the crystallinity, but it must be tied intimately to the crystal, since a macroscopic amorphous phase would crystallize. The amorphous defect, together with chain folding, could thus be identified as major causes of metastability in polymer crystals. Later research built on these initial observations.

Increasingly troublesome proved the fact that the object of my specialization, polymer science and thermal analysis, could not draw enough students at any one university at any one time to justify a full-time teaching effort. This does not mean that I did not enjoy the freshman chemistry teaching that I did regularly, but I felt that the unique knowledge that was accumulated over the years of research could not be taught in proportion to its potential value to science and industry. An experiment with the development of audio courses was made [55]. Special, condensed lectures were recorded for the audio courses and combined with books of summaries and blackboard material (equivalent to one semester, 3 credit hours, each). Although not the same as live lectures, the audio courses provided detailed instruction to anyone interested, independent of teaching schedules and location. At RPI the Evening Division handled the students, arranged for up to six hours of personal tutoring, exams, and grades. The courses ran extremely cost effective. Indeed, it would have been possible to reduce the tuition from the high private-school level and still be profitable. More than 200 students went through these audio courses at various locations. It opened the possibility for a professor to teach simultaneously at several universities and companies. The local organization would provide the students interested in the subject, schedule occasional personal visits by the author, and if needed, run tutorials and schedule exams. The experiments showed that the method works, but universities (and professors) are still too conservative to underwrite such changes in teaching methods with their wide-ranging implications.

D. Beginning of computerization and formal development of ATHAS (1975–1988)

The time period of this chapter brought a special advance in thermal analysis. Computers were added to DSC for data acquisition, treatment, and ultimately for analysis and storage in a form to give easy access at a later time (data banks). In our laboratory the modification began with adding electronic calculators with a tape or card punch for mass data storage [78]. Next, we found that expert help from computer programmers was necessary to design a fast computer that could do both acquisition and calculation of data [79]. Later, the manufacturers introduced their own, proprietary software. This latter development may have hampered independent programmers to create the specialized, more transparent software that is needed for many scientific applications. In a workshop at the 8th ICTA in Bratislava this problem was discussed and suggestions were made, but largely ignored by all manufacturers of DSCs [80]. Today it is still not easy to link the DSC output directly to data banks, thermodynamic function generators, and independently developed or acquired mathematics packages.

The introduction of affordable personal computers of the Apple, Comodore, and Atari trade marks at about 1980 did not only provide entertainment with games. These personal computers were also ideally suited to produce sound and pictures for instruction in thermal analysis in the form of computer courses [81]. All that was needed was 32 kB of RAM. After more than 10 years these programs still run on the old computer in our laboratory. They included lectures, exercises, and exams. Unfortunately none of the later computers can read the earlier figures or produce the sound. A more mature computer generation is just now developing, and its potential for teaching is discussed in Section E.

The research during this time period at RPI is documented in about 140 publications and centered around the idea of generating better thermal analysis and making fullest use of the emerging computer capabilities. The summary starts with the Advanced THermal Analysis System, ATHAS, lists the analyses of a number of new glassy and crystalline polymers, and ends with a major effort to understand mesophases.

The idea of ATHAS is rather simple. It is based on the knowledge gained with the early analysis of the heat capacity of polyethylene as detailed in Sect. B. To extend this initial effort to other polymers, we created a critically reviewed data bank of experimental heat capacities [82]. All data in the literature were uniformly presented in data tables, compared to parallel measurements, and judged for precision. This data bank is still actively growing and presently readied to be available over the internet (WWW) [83]. Having just an archival data bank was, however, not our goal. The data bank was to be the base for further advances. Figure 12 illustrates the scheme followed for the analysis of the heat capacity of solids that are expected to have mainly vibrational contributions to the heat capacity. First the C_p needs to be changed to C_v. Since the thermodynamic relationship:

$$C_p = C_V + TV\alpha^2/\beta \qquad (5)$$

requires information on expansivity α and compressibility β, quantities that are often not available for a given polymer, we adapted the Nernst-Lindemann equation to polymers as:

$$C_p - C_V = 3RA_oC_pT/T_m^o \qquad (6)$$

where A_o can either be fitted to limited experimental α and β data, or taken as a universal constant of 3.9×10^{-3} K mol J^{-1} [84]. The next step was the computation of the heat capacity contribution of the group vibrations using information based on infrared and Raman spectra. The calculation involves mainly Einstein functions [16] and combinations of one-dimensional Debye functions [17]. Subtraction of this contribution from C_v yields the experimental skeletal heat capacity. The inversion of the skeletal heat capacity gives the parameters of the Tarasov function, Θ_3 and Θ_1 [18]. The computation programs and a discussion of the results are given in [85]. The value of Θ_3 represents approximately the upper frequency limit of the intermolecular vibrations and Θ_1, the upper limit of the intramolecular chain vibrations. This analysis accounts for the left half of Fig. 12. By carrying out the computations in reverse, as indicated by the right half of the figure, C_p due to the vibrations in the solid can be calculated at any temperature. Figure 4 shows the results of such a computation. Starting at about 250 K an increasing deviation from the vibrational heat capacity occurs. It could later be linked by molecular dynamics simulation to defects in the crystal (see Sect. E). Analyses for more than 100 polymers are now available in the ATHAS Data Bank [83]. Starting with 1981, a biannual ATHAS Report was issued, describing the progress in thermal analysis. The present eighth report of 1995 concludes this series. Further information is available as soon as it happens through the WWW [83].

The theoretical description of heat capacities of liquids was attempted based on statistical mechanics approximations, but did not lead to simple analyses [86]. Liquid polymers and solid polymers with insufficient experimental data, as well as copolymers and blends are better analyzed using empirical addition schemes based on group contributions [87]. Overall, heat capacities are with these methods predictable to 3–5% precision. Once the analysis is completed,

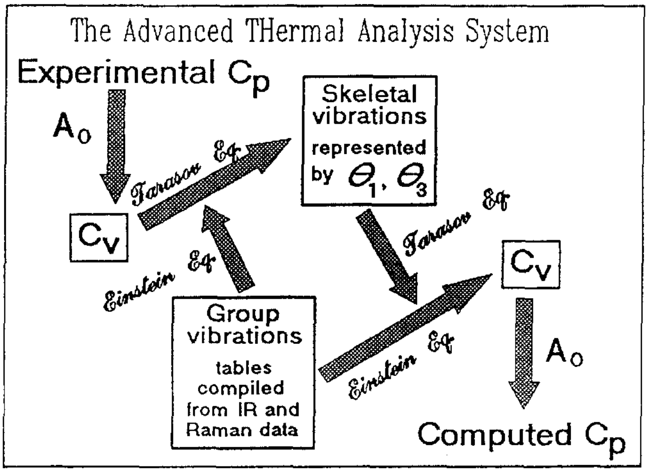

Fig. 12 The system developed for the computation of heat capacities of solids

the integral thermodynamic properties can be evaluated, as shown in Fig. 5. The needed transition parameters are usually measured independently and extrapolated to equilibrium. A listing of the presently best available information is also contained in the data bank [83].

The study of glassy polymers involved di- and tri-block copolymers of styrene and α-methyl styrene and a comparison with a blend of the same chemical composition [88]. A number of noteworthy observations were made. First, in the microphase-separated block copolymers the glass transitions were broadened asymmetrically. The upper end of the glass transition of the polystyrene phase (T_g =373 K) is due to material surrounded by the glassy poly(α-methyl styrene) and T_g is spread to higher temperature, while the beginning of the glass transition of poly(α-methylstyrene) (T_g =441 K) is due to material that is surrounded by polystyrene melt, its T_g is shifted to lower temperature. In the limit, both transitions merge and cover the full 68 K between the two transitions. The blend of the same two components as homopolymers was compatible at low and incompatible at high molar masses. The glass transition could be used for evaluation of partial or full phase separation. The glass transition of the solution was shifted to an intermediate temperature, but it was also broadened symmetrically. This broadening of the glass transition of polymer solutions is an observation that can be made also on polymer solutions with low molar mass solvents. Only if the two components are fully mixed, as in a random copolymer, is the glass transition as sharp as in homopolymers [89]. The symmetric broadening may result from the remaining unmixed neighbors along the chain direction, i.e. homopolymers in solutions remain unmixed in one dimension.

Poly(tetrafluoroethylene), PTFE, is a polymer that crystallizes easily, so it was difficult to observe its glass transition. A search of the literature indicated 36 different T_gs spread over 300 K. Quenching a PTFE copolymerized with a small amount of hexafluoropropylene led to a sample of only 17% crystallinity. With help of the data bank heat capacities, a broad glass transition centering about 200 K could be identified [90]. This was one of the first times the utility of the data bank was made use of. With the limiting heat capacities of both liquid and solid well established, the glass transition can be identified even if it spreads over more than 100 K.

The glass transitions of partially crystalline polymers are of particular interest. An analysis of poly(ethylene terephthalate) and several other polymers showed that the hysteresis observed on slow cooling followed by fast heating did not occur on most of the semicrystalline polymers [91]. In addition, the increase in heat capacity at T_g was often reduced more than expected from the independently measured crystallinity. This means that above the glass transition temperature the heat capacity is less than expected [91]. This observation was quantified on poly(oxymethylene) and the missing melt was called the "rigid amorphous fraction" [92]. The rigid amorphous fraction has later proven to be of great importance in the understanding of mechanical properties. It gives a quantitative measure of a distinct third phase in partially crystalline polymers, and expands on the concept of the nanophase-size "amorphous defects" [21].

The first sabbatical in this time period was spent to summarize the knowledge about melting by writing Volume 3 of Macromolecular Physics [93]. Also, an extensive review of the basis of thermal analysis was prepared [94], and besides updates of the audio courses [55], a computer based freshman chemistry lecture and workbook [95] were completed. The aim of the latter was to introduce students very early to the applied side of chemistry by teaching the understanding of engineering applications through polymer and solid state knowledge.

With new insight gained from scholarly work, new observations on the glass transition, and the backing of the growing data bank, many polymers were analyzed from 1975 to 1988 using the ATHAS. Much more information could be extracted from thermal analysis because of the ability to understand the irreversible transitions as shown in Fig. 9, the knowledge of the equilibrium limit, the quantitative information on C_p due to vibrations only, and the measured or extrapolated liquid C_p. The polymers studied covered a wide range. There was the inorganic polymer selenium [96] with its intriguing chemical reactions that allow chains to rearrange and change into rings, and the two-dimensional polymers of the group IV chalcogenides [97] which need to be described with a two-dimensional frequency spectrum. The basic, flexible macromolecules polyethylene [98], poly(ethylene terephthalate) [99], poly(4-methyl-1-pentene) [100], poly(oxyethylene) [101], fluoropolymers [102], and polypropylene [103] were revisited to improve the data bank and to establish transition parameters. A series of more modern, stiffer-chain molecules were analyzed, including polyparaxylylene [104], poly(oxy-1,4-phenylene-oxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK) [105], poly(oxy-2,6-dimethyl-1,4-phenylene) [106], poly(ethylene-2,6-naphthalene dicarboxylate) [107], poly(butylene terephthalate) [108], and poly(thio-1,4-phenylene) [109]. Much new understanding could be derived from this different group of polymers.

The newest class of polymers of this time period were macromolecular liquid crystals, LCs. Macromolecular LCs were first observed in form of lyotropic[1] systems [110] and discussed in terms of segmental rigidity [111]. When thermotropic, polymeric LCs[2] that need no solvent were mentioned in the scientific literature [112], it became of interest to find the similarities and differences to small-molecule LCs. Naturally, our data bank was ideally suited to form the basis for a detailed thermal analysis. We started first with a number of thermal analyses and tried to understand the new properties, such as LC glass

---

[1] Lyotropic liquid crystalline phases derive their anisotropy from interactions with solvents.

[2] A thermotropic LC has an LC/isotropic phase transition temperature at T_i, in contrast to a lyotropic LC that usually does not lose its structure at higher temperature.

transitions, heat capacities, and ordering and disordering transitions [113]. This was followed with a review of the subject that led to the discovery that many of the macromolecules classified as LCs belonged actually into a different, new type of mesophase, the "conformationally disordered phase" in short, the "condis phase" [114]. This new phase was obvious when applying the general "rules for the entropies of fusion based on molecular shape and flexibility" that were discovered when researching Vol. 3 of Macromolecular Physics [93]. The rules are listed in Fig. 13 together with "a system of classifying phases and mesophases." The condis phase is closer to the crystalline state since it has no positional and orientational disorder of the molecule as a whole. The conformations are locally mobile and disordered. They change by jumping between the different rotational isomers. Overall, this leads to the possibility of easier diffusion along the chain direction as needed for chain extension as discussed in Sect. C. The importance of this discovery led me to spend my fourth sabbatical in 1986/87, with the help of a Humboldt Prize, at the Universities of Freiburg and Ulm (Germany). Many discussions and research projects were undertaken to learn the intricacies of the condis phase. The experience of this year is summarized in Reference [61] and a series of papers were published that deal with the differences between the mesophases [115]. On my return from Germany, I was offered my present position and chose early retirement at RPI as of Jan. 1, 1988 after almost 25 years of service.

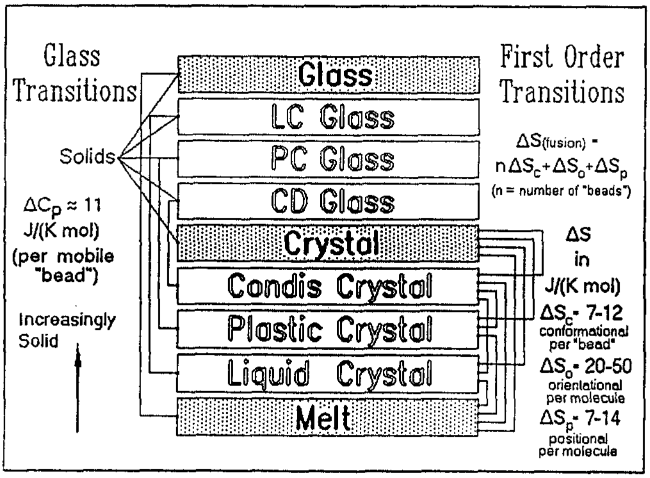

Fig. 13 The rules that govern entropies of transition and the schematics of the condensed phases

E. Molecular motion and disorder (1988–today)

It was said in the Introduction that time goes fast. This must be true since it seems like yesterday that we moved ATHAS from RPI to The University of Tennessee and Oak Ridge National Laboratory. With only one student, A. Xenopoulos, research was begun from scratch. By now this work is documented in more than 150 papers. The new teaching effort has produced a textbook on thermal analysis [116] and a new, existing method of teaching using text, figures, and hypertext displayed by computer. The latter is available over the WWW [117].

Thermal analysis is at present in a stage of rapid development, brought about by the introduction of faster and more precise calorimetric measurements and data analyses. The measurement of heat capacity by DSC has always been troubled by the need to make a series of three runs: first a base-line scan of the two empty differential calorimeters (empty sample and reference pans), to be followed by a calibration scan (usually with sapphire), and then concluded by the sample run. For critical work this should even be followed by a repeat of the base-line scan to be assured that nothing has changed during the first three runs. The main problem of calorimetry is invariably the difficulty to control heat losses. As an improvement we developed a single-run instrument based on a commercial triple calorimeter [118]. After initial calibration of the asymmetry of the three pan positions, a single run could produce good heat capacities.

A much more revolutionary approach was offered by modulation of the DSC. The sample temperature, T_s, and the temperature difference, ΔT, show in this case a small, sinusoidal variation of frequency ω [119]. Typical modulations of T_s are 0.1 to 1.0 K at 0.1 to 0.01 Hz. In this way any heat loss with a different frequency can be eliminated. Figure 14 illustrates the method of modulation with a comparison between the two methods. The details of mathematical descriptions and applications are being developed [120]. Of importance

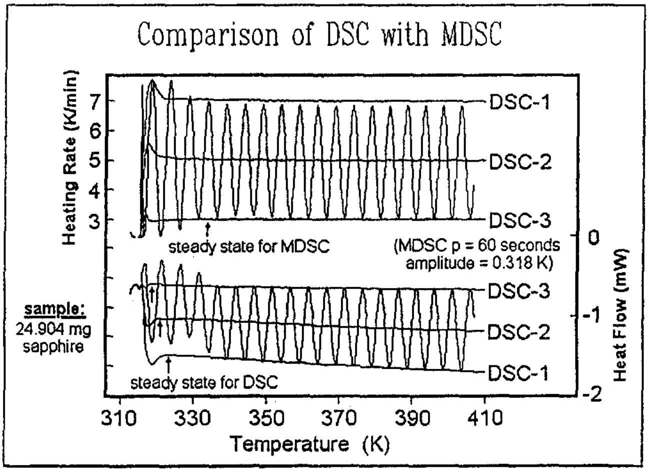

Fig. 14 Comparison of three DSC runs chosen to match maximum, average, and minimum heating rates of an MDSC run

was the proof that steady state can be achieved even in the presence of modulation when e^{-Kt/C_s} becomes negligible:

$$T_s(t) - T_o = q\left[t - \frac{C_S}{K}(1 - e^{-Kt/C_s})\right] + A_{T_s}\,[\cos\varepsilon \sin\omega t - \sin\varepsilon\cos\omega t + \sin\varepsilon\, e^{-Kt/C_s}] \tag{7}$$

where $T_s(t)$ is the time-dependent sample temperature, T_o, the starting temperature, q, the underlying, constant heating rate, C_s, the C_p of the sample calorimeter (pan +sample), K is the thermal conductivity constant, and ε is the phase shift relative to the block temperature, expressed by:

$$\sin\varepsilon = \frac{\omega}{\sqrt{\left(\frac{K}{C_S}\right)^2 + \omega^2}} \tag{8}$$

The heat capacity can then be extracted from the maximum amplitudes A of the modulation, as set for the sample temperature T_s, and measured for the temperature difference ΔT:

$$(C_S - C_r) = \frac{A_{\Delta T}}{A_{T_s}}\sqrt{\left(\frac{K}{\omega}\right)^2 + C_r^2} \tag{9}$$

where C_r is the heat capacity of the reference calorimeter (empty pan). Besides measurement of heat capacity, it is also possible to distinguish between thermal processes that occur equally on heating and cooling (such as C_p), and others, that do not (such as crystallization/melting). The temperature modulation of DSC is thus an important new technique for the study of the many irreversible processes in polymeric materials described in Sects B–E [120].

The prior research period closed with the discovery of the importance of conformational motion and disorder in polymers. Such increase in disorder is measured by an increase in entropy beyond that given by the vibrational heat capacity. Examples are the beginning of devitrification (Fig. 3), the introduction of defects below the melting temperature (Fig. 4), and the transitions to mesophases such as liquid crystals and condis crystals (Fig. 13). A research program using molecular dynamics simulations on crystals was developed in cooperation with Dr. D. W. Noid of ORNL. His programming skills allowed to simulate motion of up to 30 000 atoms for as long as 10^{-10}s by integrating the equations of motion from a chosen initial state. The results are given in about 35 joint publications. Over the years the simulations took almost 8 000 h of supercomputer time. The results are summarized in [45], and Fig. 15 demonstrates the results of importance to thermal analysis. In the upper left of Fig. 15 one can see the skeletal vibrations within a crystal as snapshots of segments of seven neighboring chains. The upper right plot shows the increasing concentration of *gauche* bonds that can be counted in a crystal that should ideally have only *trans* rotational isomers. The change of a *trans* conformation to a *gauche* conformation is the basic large-amplitude motion of flexible polymer backbones. The beginning of a sizeable concentration agrees with the increase in heat capacity seen in Fig. 4. The same increase in heat capacity was also found for all paraffins [48] and other polymers that have long paraffinic chain segments. Despite the relatively low *gauche*-concentration at any one time, the rate of *gauche*-bond formation per bond is enormous, as shown in the lower left of Fig. 15. The curves apply to different simulation conditions using 1 to 37 chains of $(CH_2\text{–})_{100}$ enclosed in rings of static chains (constant volume simulation) or without static rings (constant, zero-pressure simulation). The corollary of low concentration and fast rate of formation is a lifetime in the picosecond range. Combinations of two *gauche* defects lead to a kink, the long proposed, more stable point defect in polymer crystals [121]. With the help of kinks, crystal deformation can be understood better [45, 122]. The lower right drawing in Fig. 15 illustrates kink formation inside a crystal as a function of time. One can see the collision of all types of skeletal vibrations that provide the energy of defect formation. Based on such simulations, it is possible to visualize for the first time the thermal motion in crystals on a molecular scale. An overall discussion of the defect solid

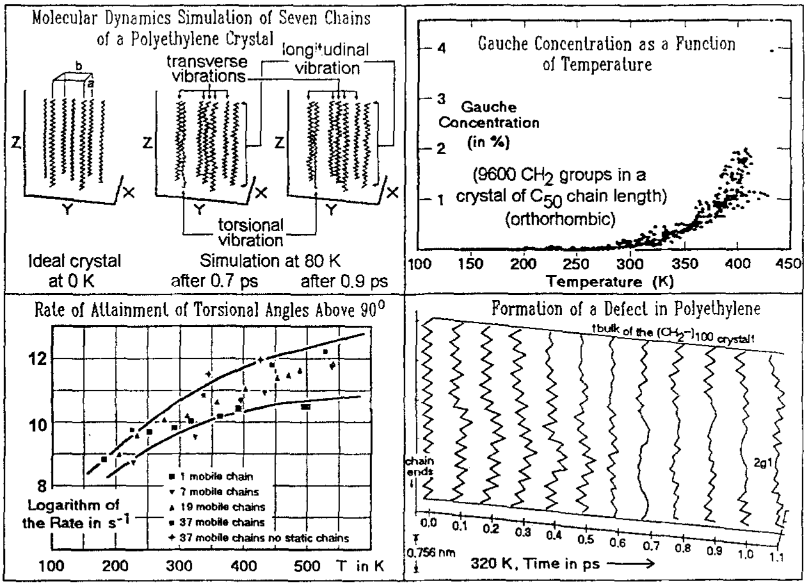

Fig. 15 Molecular dynamics simulations showing skeletal vibrations, concentration of *gauche* conformations, rate of formation of *gauche* bonds, and the mechanism of kink formation

state of polymers became thus possible, based on experiments and molecular dynamics simulations.

To support the molecular dynamics simulations, thermal analysis is the ideal macroscopic tool. To gain experience and avoid complication of excessive irreversibility known to exist in polymers, we analyzed a series of symmetric tetra-*n*-alkyl ammonium salts, known from past work to be rich in defects [74]. The calorimetry was also supported by microscopic information from ^{13}C solid state NMR to get direct experimental information on the mobility of specific atoms, and by X-ray diffraction for structure analysis [123]. Combining these results with earlier work [115] it was possible to find the signature properties of plastic crystals, liquid crystals, and condis crystals [124] (see also Fig. 13). A number of macromolecules that are located at the border between condis crystals and main-chain liquid crystals could then be identified making use of their phase structure, heat capacity, and large-amplitude mobility [125]. It was interesting to note that in many of the polymeric and small molecules which show mesophases, some of the disordering occurs outside of the transition region. Recognizing such gain of conformational disorder outside of the transition region infers that simple analyses using base-line separation of the heat capacity leads in these cases to substantial underestimation of the heats of transition.

For a long time we hesitated to study polymeric fibers by thermal analysis because of their complex structure. The observations that crystals in highly drawn fibers could persist far above the equilibrium [126, 127] was explained by the strain transmitted from the crystals to the amorphous defects (*via* tie molecules, see also Fig. 9). With the discovery of the rigid amorphous phase [91, 92] it became clear that on drawing of fibers the rigid amorphous phase

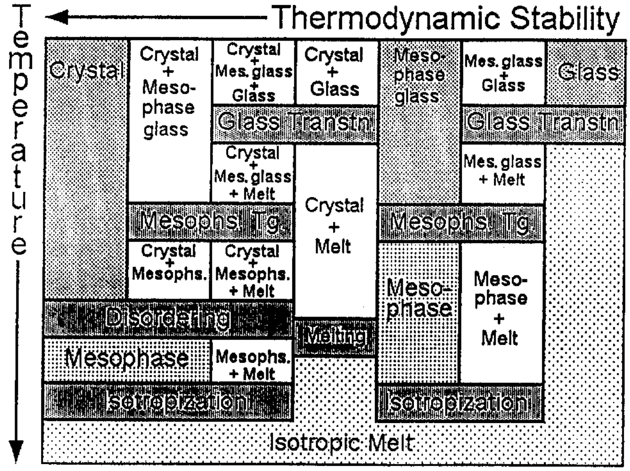

Fig. 16 Phase diagram of a three-phase system with metastable states. The equilibrium states are shown on the left

had to change its structure to an "oriented, intermediate phase." With two oriented and one amorphous phase the number of possible phase structures increases considerably, as shown in Fig. 16. Only the phases on the left side are in equilibrium. All others may appear as metastable states. Size, orientation, shape, structure, mobility, and interfaces of the phases need to be considered for the understanding of the always looked for structure-property-processing triangle.

Our work was helped by the X-ray expertise of Dr. W. Busing of ORNL. He taught us how to make a full-pattern Rietvelt analysis of the fiber diagram of, for example, poly(ethylene terephthalate) [128]. Figure 17 shows clear structural evidence of a substantial amount of an oriented, intermediate phase. Its amount and orientation are proportional to fiber modulus and tenacity. The crystallinity and the perfection of crystals are of secondary importance [128]. Another fiber that has been similarly analyzed is gel-spun ultra-high molar mass polyethylene [129]. In this case almost all polymer chains are parallel to the fiber direction, but not all participate in the crystal. By solid state ^{13}C NMR we could show that the not crystallized *trans*-chains had a much higher mobility, although less than the small amount of remaining amorphous material. Both examples documented the interrelationship of structure and mobility that are the basis of thermal analysis.

The work on the completion and computerization of the ATHAS Data Bank accelerated at UT and ORNL with the possibility to employ more permanent

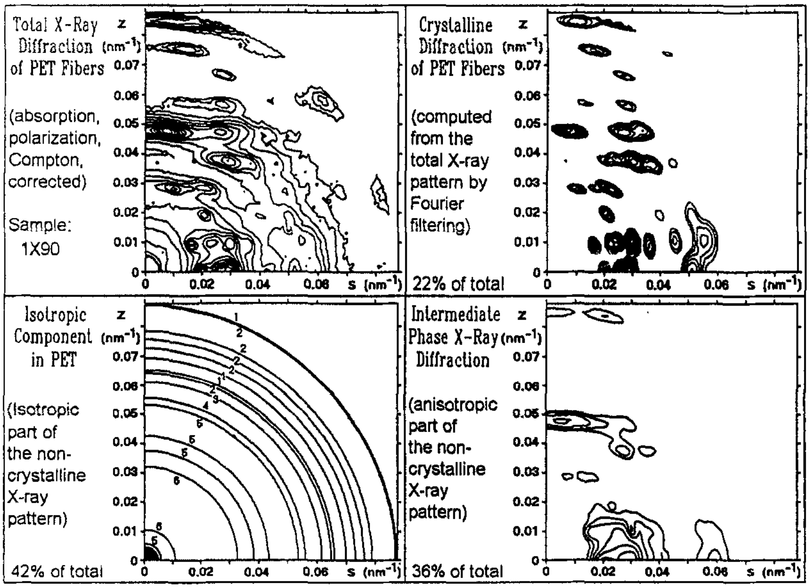

Fig. 17 Poly(ethylene terephthalate) fibers. The X-ray diffraction pattern is a superposition of the three partial patterns. (Three-phase structure)

coworkers [82]. Thermal analysis of aliphatic polyamides (nylons) [130] indicated a major increase in mobility and disorder of methylene sequences in the crystals before melting [131]. Quasi-elastic neutron scattering confirmed an almost liquid-like conformational mobility within the crystal [132]. A new direction grew out of the research about the polyamides when it was observed that the known heat capacities of a few poly(amino acids) (nylon 2) did not fit into the series of homologs [130]. The problem was resolved by remeasuring not only the few available data, but establishing information for all homopoly(amino acid)s and some copoly(amino acid)s that can be made of the 20 naturally occurring amino acids [133]. It turned out that at room temperature and above all prior measurements had up to 50% errors due to slow evaporation of water. As soon as this groundwork with poly(amino acid)s was laid, we turned to solid proteins. The first step was to find whether the ATHAS method shown in Fig. 12 is also applicable to complicated biological materials. The proof is given in Fig. 18. The root-mean-square errors of the heat capacity due to the skeletal vibrations of a protein are shown to possess a clear minimum for unique values of Θ_1 and Θ_3 of the Tarasov equation [134]. This observation opens the door for thermal analysis of proteins and allows a discussion of their stability (*G*), order (*S*), and heat content (*H*) as for polyethylene in Fig. 5.

A series of topics that may show greater importance in the future closes out this review. I have always been interested in getting to the root of problems. For crystals of polymers that meant to get a single crystal for observation. Indeed, that is possible for polyethylene [135] and some of the crystals grown during polymerization [21, Vol. 2].

Even more challenging was the effort to make single-molecule single-crystals [136]. The first crystals made proved still metastable, but it may be possible

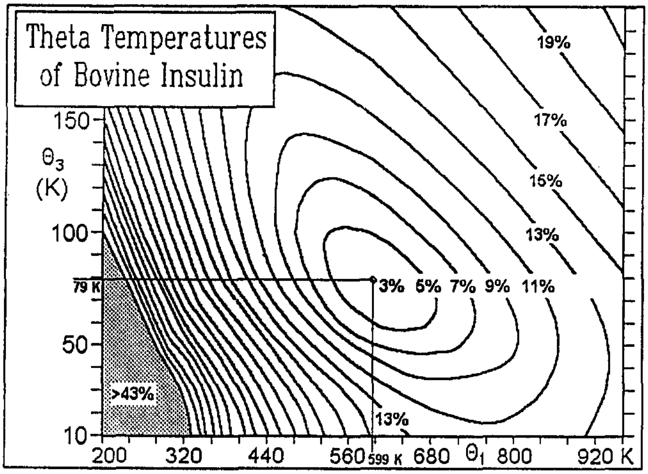

Fig. 18 Minimization of the error in description of the skeletal heat capacity of a protein. Bovine insulin $C_{508}H_{752}O_{150}N_{130}S_{12}Zn$ with a molar mass of 11 531 Da and 1553 atoms with 4659 vibrational degrees of freedom. Of these, 1256 are skeletal vibrations

to anneal them easier to the equilibrium shape. It may also be of value to see the changes when going to two or three molecules per crystal and to study how the molecular domains can fit within the confines of crystal morphology.

Direct observations of atoms is possible for a few years now by the simple method of atomic force microscopy. We bought an instrument early and could, indeed, "see" a large amount of atomic and molecular detail [137]. There is hope that this tool for nanotechnology may permit in the future to check on mechanical properties, and why not perform thermal analysis on a nanometer scale?

New materials are constantly being produced. The most exciting were the recently discovered fullerenes. We analyzed C_{60} [138] and C_{70} [139]. As one would expect, plastic crystal phases with beginning motion outside the transition region could be quantified by the ATHAS analysis. At room temperature these highly symmetric fullerenes rotate freely in the crystalline state that is stable up to very high temperatures. The large spaces between the molecules can hold molecules like toluene, with almost chemical-bond-like stability and hinder their mobility. Again, thermal analysis and solid state NMR were the tools that could easily resolve the complex behavior by quantitative interpretation of the transitions and additions to the heat capacity outside the transitions.

Thermal analysis has progressed far in linking microscopic causes to the observed macroscopic observations. Whenever such a link is well understood, predictions of the properties of new or proposed materials can be made. Sometimes these predictions are good enough to almost obviating the need for further experimentation. This leaves, however, the areas that are not supported by a well-worked-out theory. In this case it is still possible to make predictions using neural net calculations. The first attempts at neural net predictions in the field of thermal analysis showed great promise [140].

These last few items of this review point the way to the future. Much more can be done. Hopefully a good number of further developments based on the here discussed work can be seen in the future on our WWW information page [83].

F. Conclusions

Over the last 40 years much progress has been made in the understanding and techniques of thermal analysis of polymers and my students and I were very fortunate to be part of this development. Who could have predicted in the 1950s the possibility to visualize the thermal motion by supercomputer, the ability to complete the measurement of heat capacity in less than a day, the ease with which the heat capacity of proteins can be computed from its thousands of normal mode vibration frequencies, to estimate quantities for which there are no theoretical correlations (yet) *via* neural net calculations, and finally, the ability to disseminate information and teach over the World Wide Web? The field has changed and grown, but it has also become even more exciting than it was before. Thermal analysis is still one of the fastest growing discipline of research and there are many instrumental and theoretical developments that will permit increasingly more quantitative measurements and interpretations in the future.

* * *

First and foremost I would like to acknowledge the unwavering support through my wife, Heidel, without whom many of the projects simply could not have been completed. Similarly, our children had to grow up knowing that often research and teaching had to take precedence. Without coworkers, little could have been accomplished. Of the about 120 postdoctoral fellows, graduate students, and technicians, most of whom contributed to the listed references, and many have participated on their own in this issue, goes my thanks for the bulk of the scientific work. Many friends and colleagues contributed with discussion and constructive criticism, some of them have also contributed in this collection of papers related to thermal analysis. Little work can be done without this interplay of ideas. The limited space has not permitted to give a full appreciation of the importance of the ideas drawn from the literature. These thousands of additional references can be found in the initial papers and reviews of the subjects treated.

Material support was received from the three major instrument companies for thermal analysis equipment: TA Instruments, Inc.; Perkin-Elmer Corp.; and Mettler-Toledo, Inc. Without this help we would not always have been able to be at the forefront of instrumentation. Major financial support for the research came from outside the universities. I estimate that over the 40 years about 4 Megadollars were spent by government agencies, companies, and private foundations to support coworkers, myself during the summers, research equipment, expenses, and travel. A large amount of money, but not too much if one compares it to typical expenditures in the field of athletics (about 10 k$ per paper). Major sustained funding came from the Advanced Projects Agency (ARPA), the Office of Naval Research (ONR), the National Aeronautics and Space Agency (NASA), the Department of Energy (DOE), and, most prominently, the National Science Foundation (NSF). At present our work is supported by the Division of Materials Research, National Science Foundation, Polymers Program, Grant # DMR 90-00520 and the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC05-84OR21400 with Lockheed Martin Energy Systems, Inc. Industrial support is presently given by TA Instruments, Inc; ICI Paints; Exxon Res. and Eng. Co.; Shell Development Co.; Toray Research Center; and Mettler-Toledo, Inc.

Last, but by no means least, I would like to thank Dr. E. Turi for the invitation to write this paper and for her untiring effort to entice so many of my students and friends to contribute to this issue of the Journal of Thermal Analysis.

References

(The second numbers listed for the references from our laboratory refer to the overall chronolgical list of publications that contains at present (June 1995) 415 entries. For new and additional references from the ATHAS laboratory see [83]. Multiple references under one number contain a listing of all participating authors, but not everyone is necessarily a coauthor in each paper of the series.)

1 146. R. Benkhoucha and B. Wunderlich, Crystallization during Polymerization of Lithium Dihydrogen Phosphate. I. Nucleation of the Macromolecular Crystal from the Oligomer

Melt. Z. allgem. anorg. Chemie, 444 (1978) 256. 147. II. Crystal Growth by Dimer Addition. ibid., 267.
2 M. Dole, 'My Life in the Golden Age of America. 'Vantage Press, New York, NY, 1989.
3 B. Wunderlich, Thesis, Dept. Chem. Northwestern University, Evanston, IL., 1957. University Microfilms, Ann Arbor, MI, Abstract 24, 973, XVIII, 2, 1958, p. 424.
4 3. B. Wunderlich and M. Dole, Specific Heat of Synthetic High Polymers. IX. Poly(ethylene sebacate). J. Polymer Sci., 32 (1958) 125; 5. M. Dole and B. Wunderlich, Melting Points and Heats of Fusion of Polymers and Copolymers. Makromolekulare Chemie, 34 (1959) 29.
5 4. B. Wunderlich, Theory of Cold Crystallization of High Polymers. J. Chem. Phys., 29 (1958) 1395.
6 W. Nernst, Der Energieinhalt fester Stoffe. Ann. Phys., 36 (1911) 395.
7 J. C. Southard and F. G. Brickwedde, Low Temperature Specific Heats. I. An improved calorimeter for use from 14 to 300°C. J. Am. Chem. Soc., 55 (1933) 4378.
8 A. E. Worthington, P. C. Marx, and M. Dole, Calorimetry of High Polymers. III. A new Type of Adiabatic Jacket and Calorimeter. Rev. Sci. Instr., 26 (1955) 698.
9 F. E. Karasz, H. E. Bair and J. M. O'Reilly, Thermal Properties of Atactic and Isotactic Polystyrene. J. Phys. Chem., 69 (1965) 2657.
10 F. S. Dainton, D. M. Evans, F. E. Hoare, and T. P. Melia, Thermodynamic Functions of Linear High Polymers. Polymer, 3 (1962) 263, 271, 277, 286, 297, 310, 316, 317.
11 52. B. Wunderlich and H. Baur, Heat Capacities of Linear High Polymers (transl. into Russian by Yu. Godovsky, Publishing House 'Mir', Moscow, 1972). Fortschr. Hochpolymeren Forsch. (Adv. Polymer Sci.) 7 (1970) 151.
12 M. LeBlanc and M. Kröger, Die thermischen und kalorischen Größen des Kautschucks und der kautschuckähnlichen Substanzen. Z. Elektrochem., 34 (1928) 242.
13 N. Bekkedahl and H. Matheson, Heat Capacity, Entropy, and Free Energy of Rubber Hydrocarbon. J. Res. Natl. Bur. Stand., 15 (1935) 503.
14 C. T. Anderson, The Heat Capacities of Selenium Crystals, Selenium Glass, and Tellurium at low Temperatures. J. Am. Chem. Soc., 59 (1937) 1036.
15 F. T. Gucker, Jr. and W. L. Ford, The Specific Heat of 'Lucite' (Methyl Methacrylate Polymer). J. Am. Chem. Soc., 60 (1938) 2563.
16 A. Einstein, Die Plancksche Theorie der Strahlung und die Theorie der spezifischen Wärme. Ann. Phys., 22 (1907) 800.
17 P. Debye, Zur Theorie der Spezifischen Wärmen. Ann. Phys., 37 (1912) 789.
18 V. V. Tarasov, Theory of the Heat Capacity of Chain and Layer Structures. Zh. Fiz. Khim., 24 (1950) 111.
19 W. H. Stockmayer and C. E. Hecht, Heat Capacity of Chain Polymeric Crystals. J. Chem. Phys., 21 (1953) 1954.
20 The first major treatise on Polymer Science is: H. A. Stuart, 'Die Physik der Hochpolymeren. Vols. 1–4, Springer Verlag, Berlin, 1952–56.
21 For a detailed review of the crystals and crystallization of macromolecules see 95., and 102., B. Wunderlich, 'Macromolecular Physics. Vols 1 and 2.' Academic Press, New York, NY, 1973 and 1976.
22 8. B. Wunderlich and P. Sullivan, Interference Microscopy of Crystalline High Polymers. Determinations of the Thickness of Single Crystals. J. Polymer Sci., 56 (1962) 19.
23 9. B. Wunderlich and P. Sullivan, Solution-Grown Polyethylene Dendrites. J. Polymer Sci., 61 (1962) 195; 11., Interference Microscopy of Solution-grown Polyethylene Single Crystals. Polymer, 3 (1962) 247.
24 13. B. Wunderlich, The Effect of Pressure on the Crystallization of Polyethylene from Dilute Solution. J. Polymer Sci., Part A, 1 (1963) 1245.
25 17. B. Wunderlich and T. Arakawa, Polyethylene Crystallized from the Melt under Elevated Pressure. J. Polymer Sci., Part A, 2 (1964) 3697; 25. P. H. Geil, F. R. Anderson, B. Wunderlich and T. Arakawa, Morphology of Polyethylene Crystallized from the Melt under Pressure. J. Polymer Sci., Part A, 2 (1964) 3707.
26 2. B. Wunderlich and M. Dole, Specific Heat of Synthetic High Polymers. VIII. Low Pressure Polyethylene. J. Polymer Sci., 24 (1957) 201.
27 J. D. Hoffman, The Specific Heat and Degree of Crystallinity of Polychlorotrifluoroethylene. J. Am. Chem. Soc., 74 (1952) 1696.

28 K. H. Hellwege, W. Knappe and V. Semjonow, Quasistationäre Messung der spezifischen Wärme und der Wärmeleitfähigkeit an Kunststoffen. Z. angew. Phys., 11 (1959) 285.

29 F. H. Müller and H. Martin, Kalorimeter zur Messung der spezifischen Wärmen an kleinen Substanzmengen. Kolloid-Z. 172 (1960) 97.

30 M. J. O'Neill, The Analysis of a Temperature-controlled Scanning Calorimetry. Anal. Chem., 36 (1964) 1238.

31 7. B. Wunderlich and W. H. Kashdan, Thermodynamics of Crystalline Linear High Polymers. I. Comparison of the Melting Transitions of Solution and Melt-Crystallized Polyethylene. J. Polymer Sci., 50 (1961) 71.

32 12. B. Wunderlich and D. Poland, Thermodynamics of Crystalline Linear High Polymers. II. The Influence of Copolymer Units on the Thermodynamic Properties of Polyethylene. J. Polymer Sci., Part A, 1 (1963) 357.

33 16, 28 B. Wunderlich, A Thermodynamic Description of the Defect Solid State of Linear High Polymers. Polymer, 5 (1964) 125; The Melting of Defect Polymer Crystals. ibid., 611.

34 29. B. Wunderlich and D. M. Bodily, Dynamic Differential Thermal Analysis of the Glass Transition Interval. J. Polymer Sci., Part C, 6 (1964) 137.

35 23. B. Wunderlich, D. M. Bodily and M. H. Kaplan, Theory and Measurements of the Glass-transformation Interval of Polystyrene. J. Appl. Phys., 35 (1964) 95.

36 N. Hirai and H. Eyring, Bulk Viscosity in Polymeric Systems. J. Polymer Sci., 37 (1959) 51.

37 6. B. Wunderlich, Study of the Change in Specific Heat of Monomeric and Polymeric Glasses during the Glass Transition. J. Phys. Chem., 64 (1960) 1052.

38 14. B. Wunderlich, Motion in Polyethylene. I. Temperature and Crystallinity Dependence of the Specific Heat. J. Chem. Phys., 37 (1962) 1203; II. Vibrations in Crystalline Polyethylene. ibid., 1207.

39 246. H. S. Bu, W. Aycock and B. Wunderlich, Heat Capacities of Solid, Branched Macromolecules. Polymer, 28 (1987) 1165.

40 18. B. Wunderlich, Motion in Polyethylene. III. The Amorphous Polymer. J. Chem. Phys., 37 (1962) 2429.

41 21. B. Wunderlich, Motion in the Solid State of High Polymers. J. Polymer Sci., Part C, 1 (1963) 41.

42 Best summarized by: A. Lavoisier, 'Traité élémentaire de Chimie, présenté dans un ordre nouveau et d'après les découvertes modernes. Paris 1789. (Frequently reprinted, see for example the English translation of Kerr, Dover Publications, New York 1965.)

43 J. Dalton, 'An New System of Chemical Philosophy.' Manchester, England, 1808. (Frequently reprinted, see for example The Citadel Press, New York 1964, The Science Classics Library.)

44 See for example 'The Scientific Papers of J. Willard Gibbs.' Dover Publications, New York, NY, 1961 and later.

45 350. B. G. Sumpter, D. W. Noid, G. L. Liang and B. Wunderlich, 'Atomistic Dynamics of Macromolecular Crystals.' Published in the special volume on 'Atomistic Modelling of Physical Properties of Polymers' editors: U. Suter and L. Monnerie, Adv. Polymer Sci., 116 (1994) 27–72.

46 38. B. Wunderlich, Specific Heat of Polyethylene Single Crystals. J. Phys. Chem., 69 (1965) 2078.

47 36. T. Arakawa and B. Wunderlich, Thermodynamic Properties of Extended Chain Polyethylene Single Crystals. J. Polymer Sci., Part C, 16 (1967) 653; 45, 49. C. M. Cormier and B. Wunderlich, Equilibrium Dissolution Temperatures of Polyethylene and the Surface Free Energy of Folded-Chain Crystals. J. Polymer Sci., Part A-2, 4 (1966) 666; Heat of Fusion of Polyethylene. ibid., (1967) 987.

48 317. Y. Jin and B. Wunderlich, The Heat Capacity of Paraffins and Polyethylene. J. Phys. Chem., 95 (1991) 9000.

49 34 E. Hellmuth and B. Wunderlich, Superheating of Linear High-Polymer Polyethylene Crystals. J. Appl. Phys., 36 (1965) 3039.

50 43. B. Wunderlich and E. Hellmuth, Superheating Studies on Polymer Crystals. Proc. 1st ICTA, Thermal Analysis, J. P. Redfern, Ed., MacMillan and Co., Ltd., London 1965, p. 76;

66. M. Jaffe and B. Wunderlich, Superheating of Extended-Chain Polymer Crystals. Proc. 2nd ICTA. Thermal Analysis, Vol. 1, E. F. Schwenker and P. D. Garn, Eds., Academic Press, New York 1969, p. 387.

51 68, 48, 69, 47, 70, 67, 84, 89, 90, B. Wunderlich and Coworkers: Extended-Chain Crystals. J. Polymer Sci., Part A-2, 7 (1969): with T. Davidson, I. General Crystallization Conditions and Review of Pressure Crystallization of Polyethylene, p. 2043; II. Crystallization of Polyethylene under Elevated Pressure, p. 2051; with R. B. Prime III. Size Distribution of Polyethylene Crystals Grown under Elevated Pressure, p. 2061; IV. Melting under Equilibrium Conditions, p. 2073; with R. B. Prime and L. Melillo, V. Thermal Analysis and Electron Microscopy of the Melting Process in Polyethylene, p. 2091; with C. L. Gruner and R. C. Bopp, VI. Annealing of Polyethylene under Elevated Pressure, p. 2099; with M. C. Coughlin, VII. Lamellar and Fibrillar Spherulites in Selenium. J. Polymer Sci., Polymer Letters Ed., 10 (1972) 57; with L. Melillo, VIII. Morphology of Polytetrafluoroethylene. Kolloid Z. Z. Polymere, 250 (1972) 417; with M. C. Coughlin, IX. The Morphology and Mechanism of Formation of Extended-chain Crystals of Selenium. Kolloid Z. Z. Polymere, 250 (1972) 482.

52 61. B. Wunderlich, Crystallization During Polymerization. Fortschr. Hochpolymeren Forsch. (Adv. Polymer Sci.), 5 (1968) 568.

53 113. B. Wunderlich and A. Mehta, Macromolecular Nucleation. J. Polymer Sci., Polymer Phys. Ed., 12 (1974) 255.

54 53. B. Wunderlich, Differential Thermal Analysis. Physical Methods of Chemistry, A. Weissberger and B. W. Rossiter, Eds. Vol. 1, Part V. Chapter 8, p. 427, John Wiley & Sons, Inc., New York 1971.

55 108, 109, 124, 184. B. Wunderlich, Texts and Audio Courses. Crystals of Linear Macromolecules, 235 pp., Am. Chem. Soc., Washington, DC, 1973. The later audio courses were published by Rensselaer Polytechnic Institute, Troy, NY: Thermal Analysis of Linear Macromolecules, 175 pp., 1973 (second printing 1975); Crystallization of Linear Macromolecules, 225 pp., 1975; Thermal Analysis, 288+xiv pp., 1981.

56 44. B. Wunderlich and C. M. Cormier, Seeding of Supercooled Polyethylene with Extended Chain Crystals. J. Phys. Chem., 70 (1966) 1844.

57 50. B. Wunderlich, L. Melillo, C. M. Cormier, T. Davidson and G. Snyder, Surface Melting and Crystallization of Polyethylene. J. Macromol. Sci., B1 (1967) 485.

58 63 B. Wunderlich and L. Melillo, Morphology and Growth of Extended Chain Crystals of Polyethylene. Makromolekulare Chemie, 118 (1968) 250.

59 F. L. Binsbergen, A. Reconsideration of Polymer Nucleation Theory. Kolloid Z. Z. Polymere, 238 (1970) 389.

60 D. C. Bassett and B. Turner, Chain Extended Crystallization of Polyethylene: Evidence of a New High-pressure Phase. Nature (London) Phys. Sci., 240 (1970) 146.

61 200. B. Wunderlich and J. Grebowicz, Thermotropic Mesophases and Mesophase Transitions of Linear, Flexible Macromolecules. Adv. Polymer Sci., 60/61 (1984) 1.

62 263. B. Wunderlich, M. Möller, J. Grebowicz and H. Baur, 'Conformational Motion and Disorder in Low and High Molecular Mass Crystals.' Springer Verlag, Berlin 1988, (Adv. Polymer Sci., Volume 87).

63 56. M. Jaffe and B. Wunderlich, Melting of Polyoxymethylene. Kolloid Z. Z. Polymere, 216–217 (1967) 203.

64 85. S. Kubo and B. Wunderlich, Crystallization during Polymerization of Poly-p-xylylene. J. Polymer Sci., Polymer Phys. Ed., 10 (1972) 1949.

65 117. M. Mucha and B. Wunderlich, Crystallization during Polymerization of Diazomethane. I. The Boron Trifluoride Catalyzed Reaction. J. Polymer Sci., Polymer Phys. Ed., 12 (1974) 1993.

66 112. A. Mehta and B. Wunderlich, A Study of Molecular Fractionation during the Crystallization of Polymers. Colloid and Polymer Sci., 253 (1975) 193.

67 160. B. Wunderlich, Molecular Nucleation And Segregation. Disc. Farad. Soc., 68 (1979) 239.

68 228, 230, 267. S. Z. D. Cheng and B. Wunderlich, Molecular Segregation and Nucleation of Poly(ethylene oxide) Crystallized from the Melt. I. Calorimetric Study. J. Polymer Sci., Part B, Polymer Phys., 24 (1986) 577; II. Kinetics. ibid., p. 595; S. Z. D. Cheng, H. S. Bu and B. Wunderlich, III. Morphological Study. ibid., 26 (1988) 1947.

69 75, 88, 96. A. Miyagi and B. Wunderlich, Etching of Crystalline Poly(ethylene Terephthalate) by Hydrolysis. J. Polymer Sci., Polymer Phys. Ed., 10 (1972) 2073; Superheating and Reorganization on Melting of Poly(ethylene Terephthalate). ibid., p. 1401; Annealing during Polymerization of Crystalline Poly(ethylene Therephthalate). ibid., p. 2085.

70 104. M. C. Coughlin and B. Wunderlich, Polymerization during Crystallization of Selenium. J. Polymer Sci., Polymer Phys. Ed., 11 (1973) 1735.

71 114. R. Iwamoto, R. C. Bopp and B. Wunderlich, Crystallization during Polymerization of Poly-p-Xylylene. III. Crystal Structure and Molecular Orientation as a Function of Temperature. J. Polymer Sci., Polymer Phys. Ed., 13 (1975) 1925.

72 60. F. N. Liberti and B. Wunderlich, Melting of Polycaprolactam. J. Polymer Sci., Part A-2, 6 (1968) 833.

73 42. E. Hellmuth, B. Wunderlich and J. M. Rankin, Superheating of Linear High Polymers. Polytetrafluoroethylene. Appl. Polymer Symposia, 2 (1966) 101.

74 72. T. G. Coker, B. Wunderlich and G. J. Janz, Melting Mechanisms of Ionic Salts: Tetra-n-Amyl Ammonium Thiocyanate. Trans. Farad. Soc., 65 (1969) 3361.

75 78. S. M. Wolpert, A. Weitz and B. Wunderlich, Time-Dependent Heat Capacity in the Glass Transition Region. J. Polymer Sci., Part A-2, 9 (1971) 1887.

76 116. A. Weitz and B. Wunderlich, Thermal Analysis and Dilatometry of Glasses Formed Under Elevated Pressure. J. Polymer Sci., Polymer Phys. Ed., 12 (1974) 2473.

77 110. A. Mehta and B. Wunderlich, Detection of Tie-Molecules by Thermal Analysis. Makromolekulare Chemie, 175 (1974) 977.

78 130. A. Mehta and B. Wunderlich, Heats of Transition by Calculator Connected DSC. Coatings and Plastics Preprints, Am. Chem. Soc., 35 (1975) 393, 138. U. Gaur, A. Mehta and B. Wunderlich, Heat Capacity Measurements by Computer-Interfaced DSC. J. Thermal Anal., 13 (1978) 71.

79 195. B. Wunderlich, The Impact of Computers on Thermal Analysis. American Laboratory, 14 (1982) 28.

80 257. B. Wunderlich and P. Fellner, Report on the Workshop at the 8th ICTA: The Use of Computers and Data Storage in Everyday Thermoanalytic Practice. Thermochim. Acta, 110 (1987) 67.

81 204. B. Wunderlich, Computer Course and Text: Introduction to Differential Thermal Analysis, Rensselaer Polytechnic Institute, Troy, NY, 1983.

82 151–153, 159, 171, 177–180, 289. U. Gaur, H.-C. Shu, A. Mehta, S.-F. Lau, B. B. Wunderlich, M. Varma-Nair and B. Wunderlich, Heat Capacity and Other Thermodynamic Properties of Linear Macromolecules. I. Selenium; II. Polyethylene; III. Polyoxides; IV. Polypropylene; V. Polystyrene; VI. Acrylic Polymers; VII. Other Carbon Backbone Polymers; VIII. Polyesters and Polyamides; IX. Aromatic and Inorganic Polymers; X. Update of the ATHAS 1980 Data Bank. J. Phys. Chem., Ref. Data, 10 (1981) 89, 119, 1001, 1051; 11 (1982) 313, 1065; 12 (1983) 9, 29, 65; 20 (1991) 349–404.

83 Our ATHAS WWW URL is: http://tunnelweb.utcc.utk.edu/~athas. (WWW=World Wide Web, URL=Uniform Resource Locator.)

84 216. J. Grebowicz and B. Wunderlich, On the $C_p - C_v$ Conversion of Solid Linear Macromolecules. J. Thermal Anal., 30 (1985) 229.; 285. R. Pan, M. Varma and B. Wunderlich, On the $C_p - C_v$ Conversion for Solid Linear Macromolecules. II. J. Thermal Anal., 35 (1989) 955.

85 191. Yu. V. Cheban, S.-F. Lau and B. Wunderlich, Analysis of the Contribution of Skeletal Vibrations to the Heat Capacity of Linear Macromolecules. Colloid Polymer Sci., 260 (1982) 9; 207. S.-F. Lau and B. Wunderlich, Calculation of the Heat Capacity of Linear Macromolecules from Θ-Temperatures and Group Vibrations. J. Thermal Anal., 28 (1983) 59; 269. R. Pan, M. Varma-Nair and B. Wunderlich, A. Computation Scheme to Evaluate Debye and Tarasov Equations For Heat Capacity Computation without Numerical Integration. J. Ther-

mal Anal., 36 (1990) 145; 258. H. S. Bu, S. Z. D. Cheng and B. Wunderlich, Study of the Skeletal Vibrations Used to Compute Heat Capacities of Solid Macromolecules. J. Phys. Chem., 91 (1987) 4179.

86 260. K. Loufakis and B. Wunderlich, Computation of Heat Capacity of Liquid Macromolecules Based on a Statistical Mechanical Approximation. J. Phys. Chem., 92 (1988) 4205.

87. 231, 249. U. Gaur, M.-Y. Cao, R. Pan and B. Wunderlich, An Addition Scheme of Heat Capacities of Linear Macromolecules. Carbon Backbone Polymers. J. Thermal Anal., 31 (1986) 421, Part II, Backbone-chains that contain other than C-bonds. ibid., p. 1319.

88 169. U. Gaur and B. Wunderlich, Study of Microphase Separation in Block Copolymers of Styrene and α-Methylstyrene in the Glass Transition Region using Quantitative Thermal Analysis. Macromolecules, 13 (1980) 1618; 196. S.-F. Lau, J. Pathak and B. Wunderlich, Study of Phase Separation in Blends of Polystyrene and Poly-α-methylstyrene in the Glass Transition Region. Macromolecules, 15 (1982) 1278.

89 90. R. C. Bopp, U. Gaur, R. P. Kambour and B. Wunderlich, Effect of Bromination on the Thermal Properties of Poly(2,6-dimethyl-1,4-phenylene Oxide). J. Thermal Anal., 25 (1982) 243.

90 205. S.-F. Lau, J. Wesson and B. Wunderlich, The Glass Transition of Polytetrafluoroethylene. Macromolecules, 17 (1984) 1102.

91 170. J. Menczel and B. Wunderlich, Heat Capacity Hysteresis of Semicrystalline Macromolecular Glasses. J. Polymer Sci., Polymer Letters Ed., 19 (1981) 261.

92 219. H. Suzuki, J. Grebowicz and B. Wunderlich, The Glass Transition of Polyoxymethylene. British Polymer Journal, 17 (1985) 1.

93 123. B. Wunderlich, Macromolecular Physics, Volume 3, Crystal Melting Academic Press, 363 pp., New York, London, (Translated into Russian, MIR, Moscow, 1984), 1980.

94 141. B. Wunderlich, The Basis of Thermal Analysis. In: Thermal Characterization of Polymeric Materials. E. Turi, ed., Academic Press, New York, 1981, p. 91–234; revised 2nd ed., to be published 1996.

95 255. B. Wunderlich, Workbook: Chemistry 2000. Resselaer Polytechnic Institute, 306+xii pg, Troy, NY, 1987.

96 150. B. Wunderlich and H.-C. Shu, The Crystallization and Melting of Selenium. J. Crystal Growth, 48 (1980) 227; 154. H.-C. Shu, U. Gaur and B. Wunderlich, Heat Capacity and Chemical Equilibria of Liquid Selenium. J. Polymer Sci., Polymer Phys. Ed., 18 (1980) 449.

97 176. U. Gaur, G. Pultz, H. Wiedemeier and B. Wunderlich, Analysis of the Heat Capacities of Group IV Chalcogenides using Debye Temperatures. J. Thermal Anal., 21 (1981) 309.

98 139. A. Mehta, U. Gaur and B. Wunderlich, Equilibrium Melting Parameters of Poly(ethylene Terephthalate). J. Polymer Sci., Polymer Phys. Ed., 16 (1978), 289, 166. U. Gaur and B. Wunderlich, The Glass Transition Temperature of Polyethylene. Macromolecules, 13 (1980) 445.

99 139. A. Mehta, U. Gaur and B. Wunderlich, Equilibrium Melting Parameters of Poly(ethylene terephthalate). J. Polymer Sci., Polymer Phys. Ed., 16 (1978) 289.

100 144. P. C. Jain, B. Wunderlich and D. R. Chaubey, Effect of Pressure on the Melting of Poly(4-methyl-1-pentene). J. Polymer Sci., Polymer Phys. Ed., 15 (1977) 2271.

101 264. S. Z. D. Cheng and B. Wunderlich, Study of Crystallization of Low Molecular Mass Poly(ethylene oxide) from the Melt. Macromolecules, 22 (1989) 1866.

102 206. S.-F. Lau, H. Suzuki and B. Wunderlich, The Thermodynamic Properties of Polytetrafluoroethylene. J. Polymer Sci., Polymer Phys. Ed., 22 (1984) 379; 262. K. Loufakis and B. Wunderlich, Thermal Analysis of the Conformational Disorder in Semicrystalline Poly(vinylidene Fluoride) and Polytrifluoroethylene. Macromolecules, 20 (1987) 2474.

103 189. J. Grebowicz, S.-F. Lau, and B. Wunderlich, The Thermal Properties of Polypropylene, J. Polymer Sci., Symposia, 71 (1984) 19; 277. H. S. Bu, S. Z. D. Cheng, and B. Wunderlich, Addendum to the Thermal Properties of Polypropylene. Makromolekulare Chemie, Rapid Commun., 9 (1988) 75.

104 223, 224. D. E. Kirkpatrick and B. Wunderlich, Thermal Analysis of the Phase Transitions of Poly(p-xylylene). Makromolekulare Chemie, 186 (1985) 2595; On the Reversibility of

the Crystalline Phase Transitions of Poly(p-xylylene). J. Polymer Sci., Part B, Polymer Phys., 24 (1986) 931.

105 251, S. Z. D. Cheng, M.-Y. Cao and B. Wunderlich, Glass Transition and Melting of PEEK. Macromolecules, 19 (1986) 1868.

106 254. S. Z. D. Cheng and B. Wunderlich, Glass Transition and Melting Behavior of Poly(oxy-2,6-dimethyl-1,4-phenylene). Macromolecules, 20 (1987) 1630.

107 270. S. Z. D. Cheng and B. Wunderlich, Glass Transition and Melting Behavior of Poly(ethylene-2,6-naphthalene Dicarboxylate). Macromolecules, 21 (1988) 789.

108 278. S. Z. D. Cheng, R. Pan and B. Wunderlich, Thermal Analysis of Poly(buthylene Terephthalate), its Heat Capacity, Rigid Amorphous Fraction and Transition Behavior. Makromoleculare Chemie, 189 (1988) 2443.

109 256. S. Z. D. Cheng, Z. Q. Wu and B. Wunderlich, Glass Transition and Melting Behavior of Poly(thio-1,4-phenylene). Macromolecules, 20 (1987) 2801.

110 C. Robinson, Liquid Crystalline Structure in Polypeptide Solutions. Trans. Farad. Soc., 52 (1956) 571.

111 P. J. Flory, Phase Equilibria in Solutions of Rod-like Particles. Proc. Roy. Soc., A234, 60 (1956) 73.

112 A. Roviello and A. Siguru, Mesophase Studies in Polymers. J. Poly. Sci., Polymer Letters Ed., 13 (1975) 455.

113 173, 165, 192, 188, 215, 194, 293. J. Menczel, W. Meesiri, U. Gaur, J. Grebowicz, M.-Y. Cao, M. Varma-Nair and B. Wunderlich, Phase Transitions in Mesophase Macromolecules. I. Novel Behavior in the Vitrification of Poly(ethylene Terephthalate-*co*-p-oxybenzoate). J. Polymer Sci., Polymer Phys. Ed., 18 (1980) 1433; II. The Transitions of Poly(p-acryloyloxybenzoic Acid). Polymer., 22 (1981) 778, III. The Transitions in Poly(ethylene Terephthalate-*co*-p-Oxybenzoate). J. Polymer Sci., Polymer Phys. Ed., 20 (1982) 719; IV. The Glass Transition of p-Alkyl-p'-Alkoxyazoxybenzene Mesophases. J. Mol. Cryst. Liq. Cryst., 76 (1981) 287; V. Phase Transitions in Mesophase Macromacromolecules. V. The Transition in Poly(oxy-1,4-phenylene carbonyl-*co*-oxy-2,6-naphthaloyl). J. Polymer Sci., Part B, Polymer Phys., 23 (1985) 521. VI. The Transitions in PDAD. ibid., 21 (1983) 141; VII. The Thermal Properties of Poly(oxy-1,4-benzoyl), Poly(oxy-2,6-naphthoyl) and its Copolymers. Polymers for Advanced Technology, 1 (1990) 151.

114 200. B. Wunderlich and J. Grebowicz, Thermotropic Mesophases and Mesophase Transitions of Linear, Flexible Macromolecules. Adv. Polymer Sci., 60/61 (1984) 1.

115 236–239, 333, 368. B. Wunderlich, M. Möller, H. G. Wiedemann; J. Grebowicz; M. Y. Cao, J. Wesson, K. Loufakis; M. Möller, D. Oelfin; J. Cheng, Y. Jin, G. Liang and W. Chen, Condis Crystals of Small Molecules. I. The Concept and Limitations. Mol. Cryst. Liq. Cryst., 140 (1986) 211, II. The Polymorphs of N,N'-bis(4-n-octyloxybenzal)-1,4-phenylenediamine (OOBPD), ibid., 219; III. Thermal Analysis of Plastic and Condis Crystals of some Cyclosilanes, ibid., 231; IV. Solid State NMR of Cyclododecamethylhexasilane, ibid., 173 (1989) 101; V. Solid State ^{13}C NMR and Thermal Properties of N,N'-bis(4-n-Octyloxybenzal)-1,4-Phenylenediamine (OOBPD). ibid., 213 (1992) 237; VI. The Differences Between Smectic and Condis Phases, Evaluated by a Solid State ^{13}C NMR Study of N,N'-bis(4-n-octyloxbenzal)-1,4-phenylenediamine (OOBPD), ibid., 241 (1994) 299.

116 290. B. Wunderlich, 'Thermal Analysis', 450+xvi pages, Academic Press, New York, NY, 1990 (Updated figures also available on WWW, See [83]).

117 393. B. Wunderlich, 'Physical Chemistry of Polymers.' Figures, text, and hypertext of a computer-assisted course of about 1500 monitor-displayed screens. To be published on World Wide Web 1995–96 (see [83]).

118 253. B. Wunderlich, Development Towards a Single-Run DSC for Heat Capacity Measurement. J. Thermal Anal., 32 (1987) 1949; 298, 307, 331. Y. Jin and B. Wunderlich, Single Run Heat Capacity Measurements. I. ibid., 36 (1990) 765. II. Experiments at Subambient Temperatures. ibid., 1519; III. Data Analysis. ibid., 38 (1992) 2257.

119 S. R. Sauerbrunn, B. S. Crowe and M. Reading, 21st Proc. NATAS Conf. in Atlanta GA, Sept. 13–16, 1992, p. 137; M. Reading, B. K. Hahn and B. S. Crowe, US Patent 5, 224, 775 (July 6, 1993).

120 385, 378, 391. B. Wunderlich, Y. Jin, C. Schick and A. Boller, Mathematical Description of Differential Scanning Calorimetry Based on Periodic Temperature Modulation, Thermochim. Acta 238 (1994) 277; Heat Capacity Measurement by Modulated DSC at constant Temperature, J. Thermal Anal., 42 (1994) 307; Modulated Differential Thermal Analysis in the Glass Transition Range. Proc. 23rd NATAS Conf., in Toronto, Canada, Sept. 25–28, 1994. Submitted to Thermochim. Acta for publication in (1996).

121 W. Pechhold, Molekülbewegung in Polymeren. I. Teil. Konzept einer Festkörperphysik makromolekularer Stoffe. Kolloid Z. Z. Polymere, 228 (1968) 1.

122 320, 349, 384, 400. B. Wunderlich, A. Xenopoulos, D. W. Noid and B. G. Sumpter, G. L. Liang, S. N. Kreitmeier, Defect Generation and Motion in Polyethylene-like Crystals, Analyzed by Simulation with Supercomputers. In P. D. Bristowe, J. E. Epperson, J. E. Griffith and Z. Lilienthal-Weber, eds.: Defects in Materials. Proc. of the 1990 Fall Meeting of the Mat. Res. Soc., Volume 209, 1991, p. 147; Computational Experiments on the Motion and Generation of Defects in Polymer Crystals. Macromolecules, 25 (1992) 7247; Gauche Defects, Positional Disorder, Dislocations, and Slip Planes in Crystals of Long Methylene Sequences, J. Phys. Chemistry, 98 (1994) 11739; Defects in Polymer Crystals, MRS Bulletin, 20/9 (1995) 17.

123 308, 341, 325, 344, 382. A. Xenopoulos, J. Cheng, M. Yasuniwa, Q. Wang and B. Wunderlich, Mesophases of Alkylammonium Salts. I. First-order Transitions. Mol. Cryst. Liq. Cryst., 214 (1992) 63; II. Disorder and Motion in the Low Homologs: $[CH_3(CH_2(_n]_4NX$, $n=0$, 1, 2, and $X=Br$ and I. ibid., 220 (1992) 105. III. Disorder and Motion in the Intermediate Homologs $[CH_3(CH_2)_{n-1}]_4NX$; $n=4$, 5, 6, and 7; $X=Br$ and I. ibid, 127; IV. A Solid State ^{13}C NMR Study on Motion in the High Homologs $[CH_3(CH_2)_{n-1}]_4NBr$, $n=8$, 10, 12 and 18; and $[CH_3(CH_2)_{11}]_4NI$. ibid, 225, 337; V. Heat Capacities of Symmetric Halides with Alkyl Chains Longer than Ethyl. ibid., 226 (1993) 87, VI. The Crystal Structures of Tetra-n-butylammonium Bromide and Iodide, ibid., 264 (1995) 115.

124 399. B. Wunderlich and W. Chen, The Difference Between Liquid Crystals and Conformationally Disordered Crystals, Presented at the Spring 1995 ACS Meeting in Anaheim, CA, To be published in A. I. Isayev, T. Kyu, and S. Z. D. Cheng, eds. 'Recent Advances in Liquid Crystalline Polymers.' ACS Symposium Series, Washington DC, 1996.

125 334, 335, 343. J. Cheng, Y. Jin, B. Wunderlich, S. Z. D. Cheng, M. A. Yandrasits, A. Zhang and V. Percec, Solid State ^{13}C NMR Studies of Molecular Motion in MBPE-9 and MBPE-5. Macromolecules, 25 (1992) 5991, Mesophase Behavior in Thermotropic Polyethers based on the Semiflexible Mesogen 1-(4-Hydroxyphenyl) -2-(2-methyl- 4-hydroxyphenyl)ethane. ibid., 2112; Thermodynamic Functions of Thermotropic Polyethers Based on the Semiflexible Mesogen 1-(4-Hydroxyphenyl)-2-(2-methyl-4- hydroxyphenyl)ethane. Polymers Adv. Tech., 5 (1994) 785; 362. J. Cheng, Y. Jin, W. Chen, B. Wunderlich, H. Jonsson, A. Hult and U. W. Gedde, The Chain Conformations of a Polyether Based on Bis(4-hydroxyphenoxy)-p-xylylene and 1,11-Dibromoundecane (HPX-C11) in its Mesophase States, Derived from ^{13}C NMR. J. Polymer Sci., Part B: Polymer Physics, 32 (1994) 721.

126 125. G. Czornyj and B. Wunderlich, The Persistence of Birefringenece of Polyethylene Above its Melting Temperature. Makromolekulare Chemie, 178 (1977) 843.

127 283. J. Grebowicz, R. Pan and B. Wunderlich, Thermal Properties of Drawn Polytetrafluoroethylene. J. Appl. Polymer Sci., 38 (1989) 707.

128 364–366 U. Fu, W. R. Busing, Y. Jin, K. A. Affholter, A. Boller and B. Wunderlich, Poly(ethylene therephthalate) Fibers 1. Crystal Structure and Morphology Studies with Full-pattern X-ray Diffraction Refinement. Macromolecules, 26 (1993) 2187; 2. Analysis of the Noncrystalline Material in Poly(ethylene terephthalate) Fibers, Makromolekulare Chemie 195 (1994) 803; 3. Analysis of Structure and Properties of Poly(ethylene terephthalate) Fibers, J. Polymer Sci., Part B: Polymer Physics, 32 (1994) 2289.

129 390. W. Chen, Y. Fu and B. Wunderlich, The Morphology of Gel-Spun Polyethylene Fibers Investigated by Solid State ^{13}C NMR. J. Polymer Sci., Phys. Ed. 32, (1994) 2661. 404. Y. Fu, W. Chen, M. Pyda, D. Londono, B. Annis, J. Cheng, A. Boller and B. Wunderlich, Structure-Property Analysis for Gel-Spun Ultra-High Molecular-Mass Polyethylene Fibers. To be published, J. Macromol. Sci., Part B (1996).

130 281, 299. A. Xenopoulos and B. Wunderlich, Heat Capacities of Solid Polyamides. Polymer, 31 (1990) 1260; Thermodynamic Properties of Liquid and Semicrystalline, Aliphatic Polyamides. J. Polymer Sci., Part B, Polymer Phys., 28 (1990) 2271.

131 314. A. Xenopoulos and B. Wunderlich, Conformational Motion and Disorder in Aliphatic Nylons. The Case of Nylon 6.6. Colloid and Polymer Sci., 269 (1991) 375.

132 315. A. Xenopoulos, B. Wunderlich and A. H. Narten, Proton Motion in Aliphatic Nylons from Neutron Scattering. Macromolecules, 26 (1993) 1576.

133 313, 339, 340. K. Roles, A. Xenopoulos and B. Wunderlich, Heat Capacities of Solid Poly(amino acid)s. I. Polyglycine, Poly-L-alanine, and Poly-L-valine. Biopolymers, 31 (1991) 477; II. The Remaining Polymers. ibid., 33 (1993) 753; 340. Heat Capacities of Solid Copoly(amino acid)s. J. Polymer Sci., Part B. Polymer Phys., 31, (1993) 279.

134 387. G. Zhang, B. V. Lebedev and B. Wunderlich, Low Temperature Heat Capacities of Poly(amino acid)s and Proteins. To be published, J. Polymer Sci., Part B: Polymer Physics, 33 (1995) 2449.

135 133. G. Czornyj and B. Wunderlich, Preparation and Study of Separated Single Crystals of Extended-Chain Polyethylene. J. Polymer Sci., Polymer Phys. Ed., 15 (1977) 1905.

136 300. H. Bu, Y. Pang, D. Song, Y. Yu, T. Voll, G. Czornyj and B. Wunderlich, Single Molecule Single Crystals. J. Polymer Sci., Part B. Polymer Phys., 29 (1991) 139; 374. H. Bu, E. Chen, S. Xu, K. Guo and B. Wunderlich, Single-Molecule Single Crystals of Isotactic Polystyrene, J. Polymer Sci., Part B, Polym. Phys., 32 (1994) 1351.

137 336. B. K. Annis and B. Wunderlich, Atomic Force Microscopy of Extended Chain Crystals of Polyethylene. J. Polymer Sci., Part B. Polymer Phys., 31 (1993) 93; 337. B. K. Annis, D. W. Schwark, J. R. Reffner, E. L. Thomas and B. Wunderlich, Determination of Surface Morphology of Diblock Copolymers of Styrene and Butadiene by Atomic Force Microscopy. Makromolekulare Chemie, 193 (1992) 2589; 388. Q. Wang, B. Annis and B. Wunderlich, Surface Studies of Tetraalkylammonium Bromides and Iodides Using Atomic Force Microscopy. J. Polymer Sci., Part B: Polymer Physics, 32 (1994) 2653.

138 346. Y. Jin, J. Cheng, M. Varma-Nair, G. Liang, Y. Fu, B. Wunderlich, X.-D. Xiang, R. Motovoy and A. K. Zettl. Thermodynamic Characterization of C$_{60}$ by Differential Scanning Calorimetry. J. Phys. Chemistry, 96 (1992) 5151.

139 371, 372. Y. Jin, A. Xenopoulos, J. Cheng, W. Chen, B. Wunderlich, M. Diack, C. Jin, R. L. Hettich, R. N. Compton and G. Guiochon. Thermodynamic Characterization of the Plastic Crystal and Non-Plastic Crystal Phases of C$_{70}$. Mol. Cryst. Liq. Cryst., 257 (1994) 235; Motion and Disorder in the Plastic Crystal of the C$_{70}$ complex with Toluene by Solid State NMR and Thermal Analysis. ibid., 350.

140 319. J. A. Darsey, D. W. Noid, B. Wunderlich, and L. Tsoukalas, Neural-Net Extrapolations of Heat Capacities of Polymers to Low Temperatures. Makromol. Chem. Rapid Communications, 12 (1991) 325; 328. D. W. Noid, M. Varma-Nair, B. Wunderlich and J. A. Darsey, Neural Network Inversion of the Tarasov Function Used for the Computation of Polymer Heat Capacities. J. Thermal Anal., 37 (1991) 2295.